

# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XVI

NUMBER 4



October, 1943

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*Published under the Auspices of the*  
DIVISION OF RUBBER CHEMISTRY  
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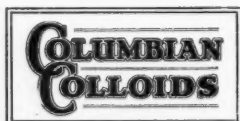
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# RUBBER CHEMISTRY AND TECHNOLOGY

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Editor.....C. C. DAVIS  
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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

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### FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, NEW YORK, N. Y.

October 5, 6, and 7, 1943

The Division of Rubber Chemistry held its Annual Fall meeting in New York City, October 5, 6, and 7, 1943, with headquarters at the Hotel Commodore. This meeting was held apart from the 106th convention of the American Chemical Society in Pittsburgh in September, because none of the available hotels in Pittsburgh could serve adequately the Division as headquarters.

The meeting, under the chairmanship of John T. Blake, proved to be one of the most successful enjoyed by the Division in recent years. For sustained attendance it surpassed previous records, with a registration of 1,150. The local arrangements were ably handled by E. B. Curtis and his committee of John H. Ingmanson, Charles R. Haynes, Walter Geldard, Harry E. Outcault, Peter P. Pinto and Brittain B. Wilson.

The following papers were presented:

1. Behavior of Carbon Blacks in Various Rubbers in a Banbury. I. Drogin, F. W. Dillingham and R. W. Grote.
2. Plastication and Processing of GR-S. G. R. Vila.
3. The Processability of GR-S and its Improvement by Chemical Means. Bernard M. Sturgis and John R. Vincent.
4. Theory of the Thermoelastic Phenomena for Rubber. Eugene Guth.
5. Mechanism of Branching During Polymerization Reactions. G. Goldfinger, W. Zybert and H. Mark.
6. Unsaturation of Polyisobutylenes and Butyl Rubber. Reactions with Nitrosobenzene, Thiocyanogen, Iodine Monochloride and Ozone. John Rehner, Jr.
7. Organic Structure of Linear Polyesters and their Rubberlike Properties. C. S. Fuller and B. S. Biggs.

8. Linear Polymer Gums: Compounding and Properties of the Vulcanizates. John K. Sumner and Robert J. Myers.
9. Measurements of the Decomposition of Peroxides in the Presence of Carbon Black. G. Goldfinger and R. P. Rossman.
10. The Effects of Blending Some Natural Rubbers with GR-S. Ross E. Morris, Arthur E. Barrett, Richard E. Harmon.
11. Solubility and Diffusion of Sulfur in Synthetic Elastomers. A. R. Kemp, F. S. Malm and B. Stiratelli.
12. Heats of Vulcanization of Synthetic Rubbers. P. D. Bruce, R. Lyle and John T. Blake.
13. Temperature Coefficient of Vulcanization of Buna-S. La Verne E. Cheyney and Robert W. Duncan.
14. A Method for the Rapid Determination of Rate of Cure of Natural and Synthetic Rubber. L. H. Cohan and M. Steinberg.
15. The Sulfur Linkage in Vulcanized Rubbers. I. The Reaction of Methyl Iodide with Sulfur compounds. II. The Reaction of Methyl Iodide with Vulcanizates. M. L. Selker and A. R. Kemp.
16. The Heat Resistance of GR-S. B. M. Sturgis, A. A. Baum and J. R. Vincent.
17. Butaprene-NF: A New Cold-Resistant Synthetic Rubber. R. H. Crossley and C. G. Cashion.
18. Compounding Study of Channel Black and M. R. in GR-S. H. F. Schwarz.
19. Effect of Variable Sulfur-Accelerator Levels on Properties of GR-S Tread Stocks. L. R. Sperberg.
20. The Effect of Time and Temperature of Cure on the Properties of GR-S Tread Stocks. A. E. Juve and B. S. Garvey, Jr.
21. Tread Cracking of Natural and Synthetic Rubber Stocks. Iven B. Prettyman.
22. Buna-S for Wire Insulation. J. H. Ingmanson, J. B. Howard, V. T. Wallder and A. R. Kemp.
23. The Sunlight Resistance of Hycar-OR Compounds. B. S. Garvey, Jr. and R. A. Emmett.
24. The Evaluation of Low-Temperature Properties of Several Synthetic Rubbers in Aviation Fuels, Using the Dyne Tensiometer. R. G. Chollar, G. J. Wilson and B. K. Green.
25. Resistance of GR-S Vulcanizates to Various Types of Aging. A. M. Neal and P. Ottenhoff.
26. Young's Modulus and Brittleness of Natural and Synthetic Elastomers at Low Temperatures. John W. Liska.
27. A Method of Measuring Low-Temperature Modulus Change in Vulcanized Elastomers. D. J. Buckley and A. L. Chaney.
28. A New Apparatus for Determining Hardness and Creep of GR-S and Rubber Compounds at Various Temperatures. J. A. Talalay and R. E. Gladstone.
29. On the Influence of Electric Fields on Rubber Latex. Eugene Guth. and I. Walerstein.
30. The Role of Carbon-Black Surface Chemistry on Reinforcement of Butyl Polymers. R. L. Zapp.

Colonel Bradley Dewey, U. S. Rubber Director, War Production Board, spoke at the Divisional banquet at the Commodore Hotel, Wednesday evening. Colonel Dewey attributed the "miracle" of the present synthetic rubber pro-

gram to the genius and devotion of American chemists, chemical engineers, and rubber technologists, and the wholehearted coöperation of the rubber industry in sharing all trade secrets and "know-how" in what had been one of the most competitive fields in peace time. The attendance at the banquet set a record at 1,070.

In the business meeting, held Thursday afternoon, W. H. Cope, Chairman of the Teller's Committee, announced the election of the following officers for 1943-1944:

Chairman.....	Harold Gray
Vice Chairman.....	W. A. Gibbons
Secretary.....	H. I. Cramer
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Sergeant-at-Arms....	B. R. Silver
Directors.....	J. T. Blake, W. W. Vogt, J. H. Doering, G. S. Haslam, A. H. Nellen.

The chairman reported: (1) that the Treasurer's books had been audited and approved by a committee headed by Verne Smithers, and (2) that the membership in the Division had passed the 1,000 mark during the last six months.

The Chairman-Elect, Harold Gray, announced that, while the Executive Committee was proceeding with plans for the Spring Meeting, no selection of meeting place had been made. This information will be published at the earliest possible date.

H. I. CRAMER  
Secretary

## NEW BOOKS AND OTHER PUBLICATIONS

A SURVEY OF THE LITERATURE ON SYNTHETIC RUBBER, WITH SPECIAL REFERENCE TO ITS HISTORY, RAW MATERIALS EMPLOYED AND ITS COMMERCIAL PRODUCTION. By Ellis I. Fulmer. Published as a Contribution from the Iowa Corn Research Institute by the Iowa Agricultural Experiment Station, Ames, Iowa. 7 x 10 in. 62 pages. 15c.—A summary of the scientific literature on synthetic rubber, with special emphasis on its history, raw materials employed in its manufacture, and data on its commercial production in various countries. The references chosen, although far from exhaustive, furnish a typical and fairly adequate cross-section of the subject of synthetic rubber. The material is arranged chronologically, with annotations and cross-references. An appended list of references includes not only the articles reviewed, but also the literature cited. [From *The Rubber Age* of New York.]

SYNTHETIC RUBBER: ITS PRODUCTION FROM PETROLEUM, COAL, AND OTHER MATERIALS. By W. C. Holliman. Information Circular No. 7242, issued by the Bureau of Mines, Department of the Interior, Washington, D. C. 8 x 10½ in. 36 pages.—This report catalogs, for quick reference, general information regarding the chemistry and physical properties of the synthetic rubbers produced commercially in the United States and other countries. The information was taken largely from technical journals, and a five-page bibliography listing the sources is included. A good deal of general information is furnished by the report, including data on Perbunan, Hycar, Chemigum, Neoprene, Vistanex,



Butyl rubber, Flexon, Thiokol, Koroseal, Flamenol, and Agripol. Brief descriptions of some of the foreign rubber-like materials, including German Buna, Russian SKA and SKB, Polish Ker, Sovprene, Mustone, Oppanol, Ethanite, Perduren, and Vulcaplas, are given. The report should serve as excellent background material for chemists and engineers, as well as the layman. [From *The Rubber Age* of New York.]

**SYNTHETIC RUBBER—ITS INFLUENCE ON RUBBER SECURITIES.** Hirsch, Lilienthal & Co., 25 Broad St., New York, N. Y. 16 pages.—This interesting brochure analyzes in an up-to-date manner the impact of the technical and chemical achievement of the founding of our synthetic rubber industry on the future of the rubber industry and, in general, on rubber securities. Because of the possibility of the lower and stabilizing effect of synthetic rubber prices, compared with crude rubber prices during the last 30 years, securities of well-entrenched rubber companies may now be classed as "investments", a distinction they have not had in the past. It is also stated, in discussing synthetic rubber, that it is now well on its way toward establishing a place for itself—not as a substitute for crude, but as a material and product with its own identity and physical characteristics, yet superior to crude rubber in dozens of important ways. Among the other subjects covered are the Big Four and independents, large inventories now out, tires—big business, mechanical rubber goods—growing in importance, rubber invades the plastics industry, independents grow stronger, and aircraft tires—new big business. [From the *India Rubber World*.]

**CRISIS IN RUBBER.** The B. F. Goodrich Co., Akron, O. 16 pages.—As stated in the foreword, this booklet is not offered as a scientific discussion on the chemical structure of rubber, but reviews the status of natural and synthetic rubber and what has been accomplished to meet the most crucial situation that has ever confronted our nation. The discussion covers wild rubber, plantation rubber, which includes mention of the Latin American developments; domestic rubber, which refers to work with *koksaghyz*, guayule, and *cryptostegia* as a source of rubber; and synthetic rubber, in which the work of the Goodrich company is reviewed, and the properties of the leading commercial synthetic rubbers presented together with an illustrated flow chart showing the ingredients used in the production of synthetic rubbers. The booklet concludes with a synthetic rubber glossary and has inserted in the last page a copy of a small pamphlet entitled, "A Chronology of the Development of Synthetic Rubber Since 1937." [From the *India Rubber World*.]

**THE AMAZON: THE LIFE HISTORY OF A MIGHTY RIVER.** By Caryl P. Haskins. Published by Doubleday, Doran & Co., Inc., Garden City, N. Y. 6x9 in. 415 pages. \$4.00.—A general picture of the Amazon Valley, largest of the earth's watersheds, and of those portions of the South American continent which it drains, is given in this new book. The author first speculates on the formation of the land in the primeval past, traces the course of the mighty river from source to mouth, describes the geography, the jungle flora, the Indian tribes, the growth of the Inca empire, the Spanish and Portuguese conquests, and finally tells the story of rubber, with which the history of the Amazon is so closely entwined. All of this is accomplished in what might be called the first section of the book, the second and larger section being devoted to details of the political history of the six countries fed by the river: Venezuela, Colombia, Ecuador, Peru, Bolivia and Brazil.

The story of rubber (Chapter XV) is factual and well told, from the earliest record of the rediscovery of latex by Charles Marie de la Condamine in the eighteenth century to the current revival of interest in South America as a result of the Japanese conquests in the Far East. The author carefully traces the development of the early rubber manufacturing industry which led to the rubber boom in the Amazon Valley and the slow but steady growth of the plantation industry in the Far East which killed off the South American trade. Reasons for the failure of the many attempts to establish plantations based on scientific methods of cultivation in the Valley are outlined. Because of the importance of South America to our overall war effort and current interest in our neighboring republics, we believe members of the rubber industry will find this book of exceeding interest. [From *The Rubber Age* of New York.]

**THE GOODYEAR RESEARCH LABORATORY.** By David Dietz. Published by the Goodyear Tire & Rubber Co., Akron, Ohio. 6 x 9 in. 58 pages.—Issued in connection with the dedication ceremonies attendant to the formal opening of Goodyear's new research laboratory in Akron last month, this book, written by the science editor of the Scripps-Howard Newspapers, is more than just a description of the new laboratory, since it briefly embraces the story of rubber and the story of Goodyear. In addition, it covers some of the research achievements credited to Goodyear scientists over the years. The description of the laboratory itself is confined to a few pages, detailing some of the equipment currently installed and the objectives planned for it. [From *The Rubber Age* of New York.]

**THE CHEMISTRY OF LARGE MOLECULES.** Edited by R. E. Burk and Oliver Grummitt. Published under the auspices of Western Reserve University by Interscience Publishers, Inc., 215 Fourth Ave., New York, N. Y. 6 x 9 in. 313 pages. \$3.50.—It is the custom for universities and colleges to have a small number of professors who may be specialists in certain fields, such as physical, organic, inorganic, and analytical chemistry, but one or a few professors in each of these fields can no longer hope to master the entire field, nor therefore to present a well-proportioned impression of the subject to graduate students.

To meet this difficulty, Western Reserve University recently conceived the idea of inviting distinguished scientists in the field of chemistry and closely related fields to be "professors for a day". Each of these men presents two lectures, giving him an opportunity to present a substantial view of his work. This book, the first volume in a series to be presented under the title of "Frontiers in Chemistry", is the result of some of those lectures.

The book consists of 8 articles, or lectures, each contributed by an outstanding expert: (1) The Mechanism of Polyreactions, by H. Mark; (2) The Investigation of High Polymers with x-Rays, by H. Mark; (3) The Colloidal Behavior of Organic Macromolecular Materials, by Elmer O. Kraemer; (4) The Ultracentrifuge and Its Application to the Study of Organic Macromolecules, by Elmer O. Kraemer; (5) Elastic-Viscous Properties of Matter, by Arthur Tobolsky, Richard E. Powell, and Henry Eyring; (6) The Electrical Properties of High Polymers, by Raymond M. Fuoss; (7) Organic Chemistry of Vinyl Polymers, by C. S. Marvel; (8) Chemistry of Cellulose and Cellulose Derivatives, by Emil Ott. The corporate affiliations of these experts is too well known to bear repetition here.

From the subject matter of each article, or lecture, it will be noted that, although each contributor has furnished data on some specific phase, the whole

represents a complete discourse on the chemistry of large molecules. Bibliographies are furnished at the end of each chapter by each author. A complete subject index has been provided by the editors, who have also included pictures of the lecturers and short biographical sketches about each of them to compensate in part for the reader's lack of personal contact, enjoyed by the participants of the lectures themselves.

Western Reserve University is to be complimented for the origination of the "professor for a day" idea, and for sponsoring the publication of the lectures in book form. [From *The Rubber Age* of New York.]

**PERBUNAN: COMPOUNDING AND PROCESSING.** (2nd Edition). Stanco Distributors, Inc., 26 Broadway, New York, N. Y. 8½ x 11 in. Looseleaf.—The second edition of this compounding and processing manual is a decided improvement over the first one, issued in April, 1942. In the first place it naturally contains more technical data, based on new information secured as a result of practical compounding and, in the second place, it is divided into sections, separated by tab sheets, so that any desired information may quickly be located.

There are nine sections in the new manual, as follows: Processing; Softeners; Fillers and Pigments; Accelerators; Mixtures with Rubber and Other Polymers; Resistance to Solvents, Oils and Petroleum Fuels; Resistance to High and Low Temperature; Miscellaneous Properties; and Product Compounding. In addition, there is a short discussion on the basic compounding of Perbunan.

The new edition contains also a special section on the compounding and processing of GR-I (Butyl), the disclosure of which is now permitted by the U. S. Patent Office modification of the existing secrecy order, although distribution of the information is carefully controlled. [From *The Rubber Age* of New York.]

**CARBON BLACK IN GR-S.** H. E. Simmons, Office of the Rubber Director, Washington, D. C. 44 pages.—This bulletin represents a summary of a report of more than 350 pages entitled "A Survey Study of Carbon Blacks in GR-S," prepared by B. S. Garvey, Jr., and J. A. Freese, Jr., of The B. F. Goodrich Co., Akron, O., and given limited distribution in March, 1943. The Educational Committee of the Office of the Rubber Director, with the advice and detailed help of the authors, has prepared this new bulletin so that the rubber industry as a whole might have the benefit of this comprehensive piece of laboratory work. Garvey and Freese have classified the various carbon blacks into groups according to approximate particle size and method of production, and the blacks are designated wherever possible in accordance with the recommendations of the Carbon Black Nomenclature Committee. Details of the experimental procedure for the determination of plasticity, tubing index, tensile, heat build up, rebound, high temperature tear resistance, hardness, and abrasion resistance are first given, after which the treatment of data, selection of cure for tensile properties, and a summary of results are stated. Included in the summary of results is a table of loading ranges for best processing properties for eight types of black and also a discussion of loading ranges for tensile and elongation. The main body of the bulletin contains bar graphs showing the effect on the above-mentioned physical properties of eight types of black in loadings from 20 to 75 PHR and line graphs for six loadings of each of the same eight types of black. The bulletin is concluded with photographs of carbon black types *versus* extrusion properties. [From the *India Rubber World*.]



**THE IMPROVEMENT IN THERMAL SHORTENING AND FATIGUE (CUT GROWTH) OF GR-S TREADS.** Columbian Carbon Co., 41 E. 42nd St., New York, N. Y. May, 1943. 36 pages. A new compounding approach to the problem of improving the resistance of GR-S treads to cut growth, based on the use of large amounts of carbon blacks of particle sizes that reach or exceed the fineness or state of subdivision of the polymer units, in conjunction with large amounts of solvent plasticizers to increase the particle size of the polymer units, is described. The theory was developed from the fact that electron microscope studies had revealed that typical GR-S latex had polymer units much smaller than the units of natural rubber latex, and were of the order of 50 m $\mu$ , which would then require carbon blacks with a particle size in about this same range for adequate reinforcement to be obtained. Since large amounts of superfine carbon blacks produce stocks of high hysteresis, enlargement of the polymer units at the same time by large amounts of solvent plasticizers appeared to be the next step required.

The bulletin reviews factors previously reported affecting flexcrack growth in the first section on fatigue, and then describes the use of the company's "hot iron" test under the section on heat tenderness. Reinforcement theory and polymer surface are discussed in the next two sections, after which results obtained with increased softener in high Micronex-high softener combinations are given and explained. A further development, in which Statex and a coal-tar softener are used, is described under a section on cooler treads for heavy-duty service. All results are then summarized and illustrated by means of charts showing the properties of the new compounds in comparison with natural rubber tread stocks and with each other. [From the *India Rubber World*.]

**HOW TO PREVENT TIRE MISUSE.** By L. V. Bates. English Universities Press, 1943. xvi + 57 pages. Price, 2s, 6d.—This book, which is a reprint of a series of articles in the *Commercial Monitor*, with a foreword by the Earl of Rothes, Director of Tires, Ministry of Supply, presents a detailed analysis of the damage to tires by underinflation (carcass damage and external affects), overloading, misalignment, concussion, speed and braking, road surfaces, bead damage, twin-tire problems, general mechanical faults in the vehicle, load distribution, weather, including heat, neglected repair and injury, bad driving, inner-tube problems, and special operating conditions. Sections on economical mileage limits and general maintenance and equipment are included. There are one-hundred and four illustrations of exceptional clarity and diagnostic value to show the various kinds of damage caused by different misuses, and practical advice is given throughout on how to minimize tire wear to the greatest possible extent. Load-pressure tables are given. The work is easily the most comprehensive and illuminating discussion of the subject available, and is of exceptional value during the present crisis. [From the *Journal of Research of the British Rubber Manufacturers' Association*.]

**HANDBOOK OF PLASTICS.** By Herbert R. Simonds and Carleton Ellis. Published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 6½ x 9¼ in. 1082 pages. \$10.00.—The essential facts and figures of the entire plastics industry, still growing by leaps and bounds, are included in this monumental handbook. It presents exhaustively, yet with proper selection, the fundamental basis and technology of the industry, covering fully the present state of the field, the physical and chemical properties of plastics, their production, manufacture and finishing, and, as stated in the preface, "all of the

useful information which anyone working with plastics should find in a well organized and thorough treatment of the subject".

The book is divided into nine sections, each section being subdivided into numerous headings. The sections are: (1) Introduction; (2) Physical Properties of Plastics; (3) Materials; (4) Manufacture of Plastics; (5) Processing and Fabrication; (6) Chemistry of Plastics; (7) Application of Plastics; (8) Commercial Considerations; (9) Appendix, Glossary, Bibliography. There are numerous illustrations, schematic drawings, flow charts, etc., and 129 tables. In addition, there is a carefully cross-referenced general index.

Because the border-line between rubber and plastics becomes closer with each new discovery, it is natural that references to rubber of all types—natural, crude, reclaimed, synthetic and derivatives—crop up throughout this handbook. A complete chapter, however, is devoted to "Synthetic Rubbers and Elastomers." Classifying these rubbers into thermoplastic and thermosetting (or curing) types, the authors discuss briefly the various types, including the Bunas, Butyl rubber, Neoprene and Thiokol. A table showing the chemical structure of varieties of synthetic rubber and another giving the properties of various substances of rubbery characteristics are included in this chapter. Some examples of rubber-synthetic mixtures are discussed.

Collection of material for inclusion in this handbook was started by Simonds and Ellis early in 1940. After the death of Ellis in January, 1942, the handbook was completed by Simonds, with the coöperation of H. M. Bigelow, now a Captain in Chemical Warfare Service and formerly head of the Technical Service Division of the Plaskon Co., Inc. The coöperation of a distinguished group of representative technical men was also enlisted. It is evident from the wealth of information on plastics given by the handbook that all concerned did their work well. [From *The Rubber Age* of New York.]

A.S.T.M. STANDARDS ON PLASTICS. Prepared by A.S.T.M. Committee D-20 on Plastics and D-9 on Electrical Insulating Materials. Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. May, 1943. Paper, 6 by 9 inches. 375 pages. Price \$2.—The first edition of this new A.S.T.M. publication on plastics was prepared by Committee D-20 on Plastics and Committee D-9 on Electrical Insulating Materials, with some assistance from other groups, including Committee D-11 on Rubber Products. The book contains 71 specifications, methods of tests, and definitions on plastic materials, of which more than 20 items were developed as a result of work of Committee D-9 in the field of electrical insulation materials.

Standard specifications on the following materials are covered: several kinds of molding compounds—phenolic, polystyrene, melamine-formaldehyde, urea-formaldehyde, cellulose acetate, cellulose acetate-butyrate; also sheets, rods, etc., of cellulose nitrate, and cast methacrylate. Included also are specifications for vinyl chloride-acetate resin sheets, phenolic laminated sheets and phenolic laminated tubing for radio applications.

Standard test procedures essential in determining the various properties of plastics cover such matters as arc resistance, chemical resistance, color fastness, compressive strength, deformation, dielectric constant, flammability, flexural strength, flow temperatures, haze, impact resistance, refractive index, shrinkage, softening point, tensile properties, tear resistance, thermal conductivities, water absorption, etc.

A descriptive nomenclature is included, and there are various sets of definitions of terms of interest in the plastics field. [From the *India Rubber World*.]

**INDUSTRIAL CHEMISTRY.** (4th Edition). By Emil Raymond Riegel. Published by Reinhold Publishing Corp., 330 West 42nd St., New York, N. Y. 6 x 9 in. 861 pages. \$5.50.—The general scheme of this latest edition, which is an authoritative, readable treatise surveying all the important processes and practices of more than fifty key industries in which chemistry plays an important part, is practically unchanged from the previous edition, published in 1937. Several chapters have of course been completely rewritten, while many others have been changed, corrected and amended to bring them up-to-date. The chapter on rubber, for example, includes developments in synthetic rubber, as well as the latest advances in working natural rubber.

The chapter on rubber, which was written in close collaboration with R. B. Stringfield, well known consulting chemical engineer of Los Angeles, is typical of the treatment given to the diversity of materials covered by the book. It treats of the discovery of rubber, the growth of the plantation industry, development of vulcanization (the credit for which is granted to Luedersdorff, Hayward, Goodyear and Hancock), compounding and compounding ingredients, stock preparation, and numerous rubber products, including tires and tubes, belting, garden hose, gaskets, flooring, hard rubber, cements, sponge rubber, and reclaimed rubber.

Like the other chapters in the book, the one on rubber has a brief appendix listing the more important patents of the industry, outlining a few problems, and giving a list of reading references. In all, the book has 50 chapters, a carefully cross-referenced index, tables on chemical elements, conversions, Diesel fuel standards, and data on chemical and allied manufactures. The latest edition of this work is not only of value to the student and the teacher, but serves as a complete refresher course in industrial chemistry for chemists, physicists, engineers, and technical and scientific workers in general. [From *The Rubber Age* of New York.]

**1943 CHEMICAL FORMULARY.** Edited by H. Bennett. Published by the Chemical Publishing Co., Inc., 26 Court St., Brooklyn, N. Y. 5½ x 8½ in. 640 pages. \$6.00.—The latest edition of this work—the sixth to be published—broadens and brings up-to-date the contents of the five preceding volumes. Special elementary formulas of direct and indirect military interest have been included, while a chapter on substitutes (including rubber substitutes) has been added. The simple introductory chapter of general directions and advice, which is of value to mature users of the book who have not had previous training or experience in the art of chemical compounding, has been repeated, and a directory of sources of chemicals and supplies has been added.

Products covered in this latest edition of chemical formulas include: Adhesives; Beverages; Cosmetics and Drugs; Emulsions; Farm and Garden Specialties; Food Products; Hides, Leather and Fur; Inks and Marking Materials; Lubricants and Oils; Materials of Construction; Metals, Alloys and Their Treatment; Paint, Varnish, Lacquer and Other Coatings; Paper; Photography; Polishes and Abrasives; Rubber, Resins, Plastics and Waxes; Soaps and Cleaners; and Textiles and Fibers. A subject index is included. [From *The Rubber Age* of New York.]

**SYNTHETIC ADHESIVES.** By Paul I. Smith. Published by the Chemical Publishing Co., Inc., 26 Court St., Brooklyn, N. Y. 5½ x 8½ in. 125 pages. \$3.00.—The scope of synthetic adhesives has increased by leaps and bounds during the last ten years, and there are today hundreds of different types of

cements produced to solve problems which before seemed impossible of solution. This new reference book describes the main types of synthetic adhesives, including chlorinated rubber and synthetic rubber cements, cellulose adhesives, and urea-formaldehyde glues, emphasizing their peculiar properties and major applications. The general applications of synthetic adhesives in industry are discussed, as is the use of such adhesives in the manufacture of aeronautical improved plywood and high-density woods. The book has 10 chapters and a subject index. [From *The Rubber Age* of New York.]

## THE SECOND MILE\*

L. B. SEBRELL

GOODYEAR TIRE AND RUBBER COMPANY, AKRON, OHIO

The title "The Second Mile" was inspired by an address given by W. E. Wickenden, of the Case School of Applied Science, on an entirely different subject. Since this title seemed to suit the synthetic rubber situation as it now exists, Wickenden's permission was secured to use the title in connection with this lecture. In its broader aspects, the paper purports to cover the present status of the synthetic rubber situation. Natural rubber will be compared with the copolymers made from butadiene and styrene, butadiene and acrylonitrile, and the copolymers generally known as Butyl rubber. These three materials were chosen for the comparative study because they are the materials which the Government proposes to use in the largest quantities to alleviate the present shortage of rubber. It is hoped that the data will give a fairly accurate picture of the comparative or relative values of these synthetic rubbers and natural rubber. There will be no discussion of the methods of manufacture, which are still more or less secret. It is proposed also to go into the probable structure of these polymers and to indicate some trends of research which might profitably be followed to improve them.

### POLYMERIZATION

The polymerization of organic substances has been known for considerably more than a hundred years. Berzelius<sup>1</sup> was the first to use the term "polymerization" and to define it as indicating those compounds which possess the same properties but have a different total number of atoms. Williams<sup>2</sup> is generally credited with the first preparation of isoprene when he separated this material from the products of destructive distillation of rubber. However, Himly<sup>3</sup>, while investigating the fractional distillation of rubber, isolated a distillate which he called "Faradayin". He also coined the term "Kautchin" (now known as dipentene) for one of the higher boiling fractions. However, these investigators did not again polymerize these rubberlike products to any compounds of a higher molecular weight.

Bouchardat<sup>4</sup> is usually given the credit for first synthesizing a rubber-like material from a liquid of low molecular weight. In 1875 he advanced the idea that isoprene is a primary unit of natural rubber and succeeded in producing a rubbery polymer from the distillation products by the process of polymerization. He brought about this conversion by heating isoprene with fuming hydrochloric acid and obtained a product which he described as being elastic and possessing the characteristics of rubber. Tilden<sup>5</sup> then showed that isoprene could be obtained by the pyrolysis of turpentine, and that by treatment with hydrochloric acid it would also undergo spontaneous polymerization. He also polymerized isoprene by the use of nitrosyl chloride. The work of Tilden was carried on by Hofmann<sup>6</sup> in Germany. In connection with Coutelle<sup>7</sup>, Hofmann obtained the earliest German patent on the production of synthetic

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 35, No. 7, pages 736-750, July 1943. This paper is the first Charles Goodyear Memorial Lecture, and was presented before the Division of Rubber Chemistry at the 105th meeting of the American Chemical Society, Detroit, Michigan.



rubber by the heat polymerization of isoprene with or without polymerizing agents.

In 1910 Matthews and Strange<sup>8</sup> in England and Harries<sup>9</sup> in Germany reported almost simultaneously that metallic sodium catalyzes the polymerization of isoprene to synthetic rubber. The claims of these early patents specify subjecting isoprene to metals of the alkali or alkaline earth groups, their mixtures, alloys, or amalgams in such a manner that the metals are wholly or largely in contact with the vapor of the hydrocarbon.

The story of synthetic rubber manufacture in Germany during the First World War is well known. A derivative of butadiene (2,3-dimethylbutadiene) was polymerized by means of sodium to give methyl rubber. During 1914-1918 some 2400 tons were said to have been manufactured. One or two different grades of this type of synthetic rubber were prepared at that time; almost all of the dimethylbutadiene was made from acetone.

After the First World War, several attempts were made to carry on the development of synthetic rubber in various laboratories, both in the United States and abroad. It can be said safely that not until it was generally known in the United States that the Germans were again devoting serious attention to the synthetic rubber problem was concerted effort put forth here to produce a good synthetic rubber.

In Italy the polymerization of butadiene and related hydrocarbons by the sodium method has been fairly well developed, and samples received in this country have been of a relatively high quality.

However, only after the general application of the emulsion technique of manufacturing synthetic rubbers did they begin to assume an important role in supplying large quantities of material. One of the first patents on the emulsion polymerization of synthetic rubber was granted to Dinsmore<sup>10</sup> in 1929. This was followed in 1930-1933 by patents on the emulsion polymerization of butadiene-styrene and butadiene-acrylonitrile, mixtures issued to the German chemists Tschunker and Bock<sup>11</sup>, Konrad<sup>12</sup>, and other investigators in that country. From the basic foundation of these emulsion type copolymers and variations in this technique, our entire picture of synthetic rubber has been built up. Perhaps exceptions to this statement should be made, since the polymerization of Butyl rubber does not follow this technique, and in this case a special method of polymerization has been applied, the exact nature of which has not been publicized.

#### LATEX

There is an outstanding difference in the particle size of natural latex and the synthetic latex of any of the copolymers made by the emulsion processes above referred to. Figure 1 represents natural and synthetic latex, respectively. The synthetic latex, when examined with the ordinary microscope, is of so small a particle size as to be almost invisible. The electron microscope shows the presence of particles, but these particles may be merely aggregations of larger clumps of molecules.

In discussing the difference in particle size with A. R. Kemp, of the Bell Telephone Laboratories, he pointed out that possibly the particle size of the synthetic latex might be directly connected with the physical properties to be obtained from synthetic rubbers. It is common knowledge that the present types of synthetic rubber do not give as good results when vulcanized in pure-gum stocks as they do when substantial quantities of carbon black are added.

This brings up the question of whether or not carbon black, being of sub-

microscopic size, acts as a grinding medium; and whether, on being milled with the synthetic rubber, it has a pronounced surface effect on the particles of synthetic latex or acts as a shearing medium to break them down and reveal less highly polymerized rubber in the interior of these small particles. This assumption is based on the fact that, in milling, the original latex particles are disintegrated; it has long been known that the outer shells of these particles possess a somewhat higher degree of polymerization than the interior of the natural latex particle. Further studies with the ultramicroscope may disclose additional data of value in determining the difference in particle size between natural and synthetic latex and supply the reason for the differences and the possible significance of such variations.

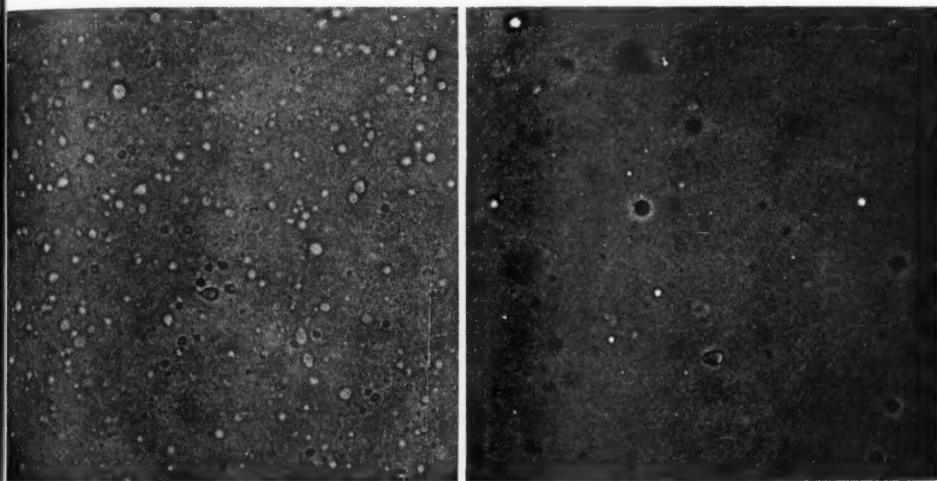


Fig. 1.—Electron micrograms of natural (left) and synthetic (right) latices ( $\times 1300$ ).

#### X-RAY STRUCTURE OF SYNTHETIC RUBBER

A considerable amount of attention has been given to the x-ray diagrams of various synthetic rubbers, but it has not been possible to apply the results of such studies directly to the process of improving the copolymer types of synthetic rubber now under consideration.

The general character of the x-ray diffraction results with synthetic rubbers was discussed in a previous paper<sup>13</sup>. The copolymers of butadiene and styrene and of butadiene and acrylonitrile are amorphous under all conditions. Polyisobutylene and polychloroprene, on the other hand, develop a crystalline structure when stretched. Stretched Butyl-B rubber shows the same crystalline structure as that of polyisobutylene. Thiokol has a somewhat crystalline structure, both stretched and unstretched.

In cases where crystalline structures are obtained, it is evident that the x-ray patterns can be used to secure information on the chain form. They can be used to evaluate in various indirect ways the strength of the intermolecular forces and the relations between molecular length, molecular length distribution, and molecular mobility, which in turn finds its reflection in the plastic properties.

The x-ray diffraction results with Butyl-B rubber are especially interesting when correlated with stress-strain curves. Figure 2 shows the amorphous pattern for unstretched Butyl rubber and the crystalline pattern which develops on stretching. Unlike *Hevea* and GR-S, Butyl rubber does not show very marked improvement in tensile strength due to incorporation of gas black, although typical reinforcement occurs for such properties as abrasion, tear, and modulus. Since the tensile strength is closely connected with the crystallinity at high elongations, x-ray diffraction results might be expected to throw some light on this apparently contradictory result.

It was found that the crystallization phenomena in loaded and unloaded Butyl rubber stocks were analogous to those with *Hevea*<sup>14</sup>. Evidence of crystallization began to appear at about 500 per cent elongation for the gum stock and at about 200 per cent for a compound loaded with 60 parts of gas black. Spreading of the diffraction spots into longer arcs for the loaded stock indicated that the alignment of the crystallites in the direction of stretching

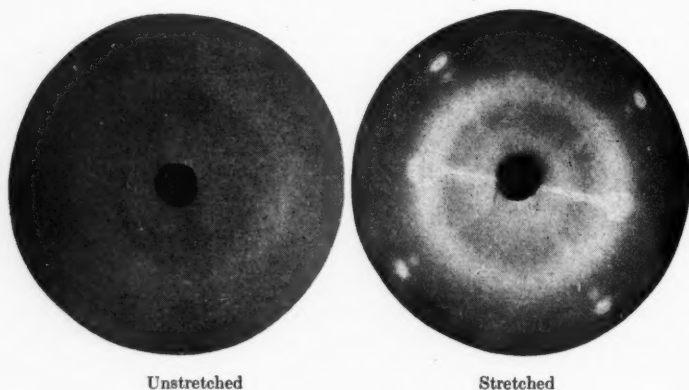


FIG. 2.—X-ray patterns of Butyl rubber.

was less perfect than for the gum stock. Thus, although higher elongations are required for crystallization in Butyl rubber compared to *Hevea*, the effect of carbon black on the patterns is similar.

The stress-strain curves in Figure 3 indicate that there may be a simple explanation of the apparent lack of tensile reinforcement. Between 800 and 900 per cent elongation, the stress-strain curve of the Butyl rubber gum stock rises abruptly, reflecting the onset of a highly crystalline structure, which is also indicated by the sharp, intense diffraction pattern. The fact that crystallization sets in at higher elongations when the molecules are already well aligned probably contributes to this perfection, as does the simple and regular chain form of the Butyl rubber molecules. Thus, in the gum stock, the ultimate tensile strength of the material is nearly realized, as a result of its own crystal reinforcement. The black can contribute little further in this respect, and its interference in the alignment of the crystallites may actually work against a higher tensile strength. For *Hevea*, on the other hand, the onset of crystallization is more gradual, and the resulting structure less regular. The black can furnish effective anchorage points to prevent failure from starting between the crystallites, and a large improvement in tensile strength results.



For copolymers, which invariably show amorphous structures, the use of x-ray diffraction as a means of investigating the molecular structure is severely limited. It is true that, even in the case of liquids, x-rays reveal a fundamental type of molecular structure which consists of a statistical space distribution of neighboring molecules. The only information to be obtained directly from the analysis of such patterns is the average distance of atom neighbors. A comparative study of these amorphous patterns of copolymers yields some interesting results, even without carrying through the involved mathematical analysis required for their exact interpretation.

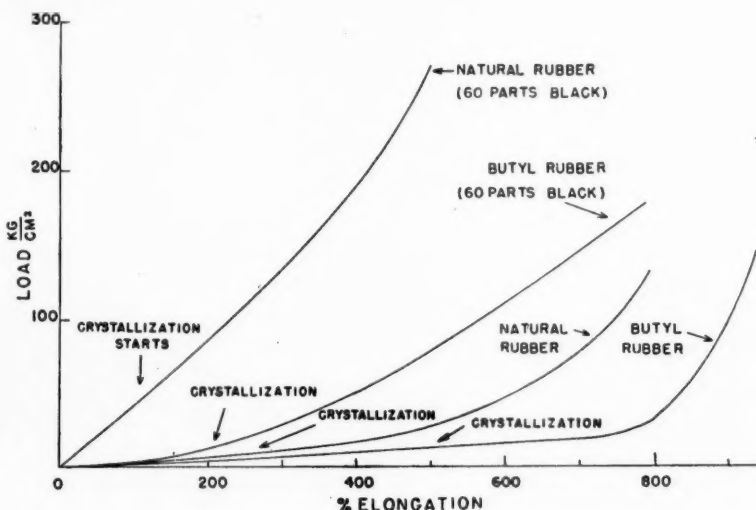


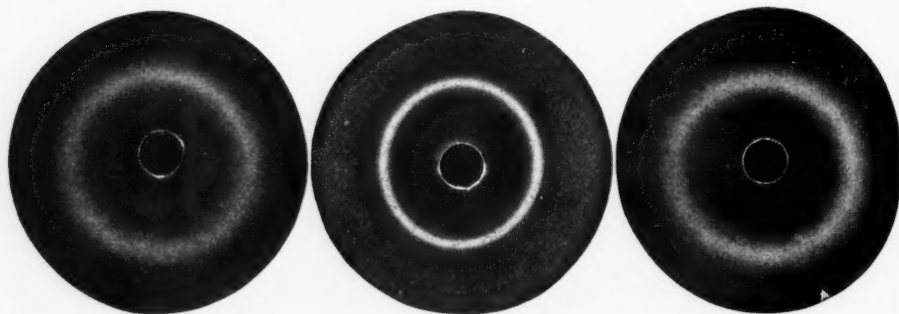
FIG. 3.—Stress-strain curve. s

The patterns shown in Figures 4, 5, and 6 were taken by J. E. Field, using strictly monochromatic  $\text{CuK}\alpha$  radiation secured by reflection of the x-ray beam from a rock salt crystal.

The polybutadiene pattern (Figure 4) is a broad halo, indicating an amorphous structure. In contrast, the pattern of polyacrylonitrile shows a sharp diffraction ring, proving the existence of small crystalline regions in random orientation. The pattern of polystyrene indicates that, in addition to the usual halo for liquids, there is an inner ring corresponding to a larger molecular spacing. Thus, these three polymers give patterns which are readily distinguishable. We wished to know to what extent these structures occurred in copolymers.

Figure 5 shows the pattern of an emulsion copolymer with a 75-25 starting ratio of butadiene to acrylonitrile. This appears to be the pattern of a homogeneous structure. When the starting ratio was 50-50, the crystalline ring of polyacrylonitrile became plainly evident. Two conclusions can be drawn. Either some or all of the acrylonitrile units of the chain molecules were sufficiently numerous and flexible to come within their normal range of action and assume the same structural relations as for polyacrylonitrile, or the polymer was not entirely a true copolymer and some polyacrylonitrile was formed during the polymerization.

The pattern from a copolymer made with a 50-50 starting ratio of butadiene to styrene (Figure 5) does not show any evidence of the inner polystyrene ring and, hence, of the polystyrene structure. The presence of the inner polystyrene ring could not be detected until the styrene component was about 70 per cent. Estimating from the completeness of the copolymerizing reaction,

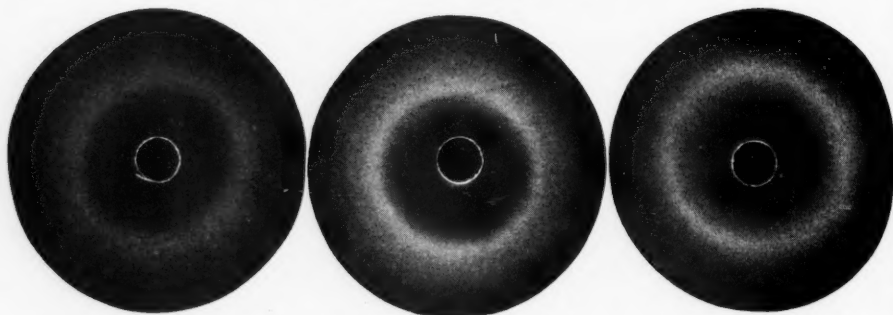


Polybutadiene

Polyacrylonitrile

Polystyrene

FIG. 4.—X-ray patterns of polymers.



75 butadiene-25 acrylonitrile

50 butadiene-50 acrylonitrile

50-butadiene-50 styrene

FIG. 5.—X-ray patterns of copolymers.

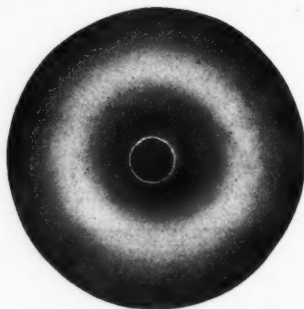


FIG. 6.—X-ray pattern of 50 butadiene-25 acrylonitrile-25 styrene.

this starting ratio was also the composition of the product. Since the molecular weight of styrene is about twice that of butadiene, this is approximately the composition for which the number of molecules of each component would be the same.

Control patterns were run on products coagulated from mixtures of polybutadiene and polystyrene latices. Thirty per cent of polystyrene could be readily detected by the presence of the inner ring. Although this method of x-ray analysis is not so sensitive as might be desired, it shows that, for copolymerization of either acrylonitrile or styrene with butadiene, the structure of polyacrylonitrile and of polystyrene, respectively, tends to make its appearance when the number of molecules approximates the number of butadiene molecules.

In an experiment with a three-component system, with starting ratios of 50, 25, and 25 of butadiene, acrylonitrile, and styrene, respectively, the pattern of Figure 6 was obtained. The presence of polystyrene structure is plainly shown by the inner halo, indicating a different character of reaction for this system compared to the two-component system.

To what feature of the polystyrene structure the inner ring is related is not definitely known. Katz<sup>15</sup> ascribed it to a large spacing of parallel molecular

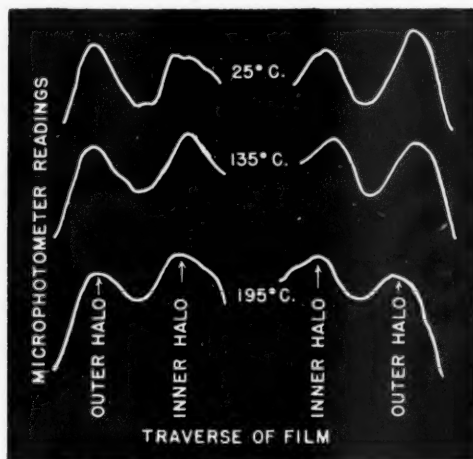


FIG. 7.—Microphotometer curves for polystyrene.

chains brought about by the attached benzene rings. To test this idea, we determined the effect of the polystyrene temperature on the relatively intensity of the inner and outer halos of the polystyrene pattern. The results are shown in the microphotometer curves of Figure 7. Curiously enough, the pattern does not approach that of monomeric styrene (a single halo) as the temperature is raised; on the contrary, the relative intensity of the inner ring is increased. At 195° C, for which a microphotometer curve is shown, the polymer had actually melted and become a viscous fluid. Thus the inner ring represents some statistical molecular configuration which is not necessarily associated with the solid state.

#### MOLECULAR WEIGHT DETERMINATIONS OF SYNTHETIC RUBBERS

The molecular weight of the butadiene copolymer with styrene was determined and compared with that of natural rubber, obtained by the same method, in the hope that this information will be of value in the preparation of an improved type of synthetic rubber. Viscosity measurements, described by

Staudinger<sup>16</sup>, were used for this purpose. The molecular weight of the butadiene copolymer was also determined by the ultracentrifuge method.

**Benzene Solubility and Swelling Indices.**—One of the readily observed differences between synthetic butadiene rubbers is their degree of solubility and swelling in solvents, such as benzene, which are good solvents for the polymer if no considerable degree of cross-linking has taken place. If the degree of polymerization, reaction temperature, or other conditions have caused appreciable cross-linkage, however, a portion of the rubber becomes insoluble in benzene, regardless of concentration or time of exposure to the solvent. The insoluble portion will be swollen to a degree dependent, in turn, on the degree of branching and cross-linkage of the insoluble fraction.

The determination of benzene solubility and swelling index involves the extraction of finely divided polymer at 35° C for 16 hours and separation of the sol and gel phases with a fine-mesh Monel screen. The solubility is determined by evaporation of an aliquot portion of the filtrate, and is expressed as per cent of the original rubber soluble in benzene.

The swelling index is defined as:

$$\frac{\text{cc. of solution retained by swollen gel}}{\text{grams undissolved rubber}}$$

and is calculated by subtracting from the original volume of the solvent the volume of the filtrate and dividing by the weight of undissolved polymer.

The swelling indices were determined for a large number of butadiene-styrene rubbers of varying benzene solubilities. A good correlation was found for these values, as Figure 8 shows. As would be expected, the insoluble

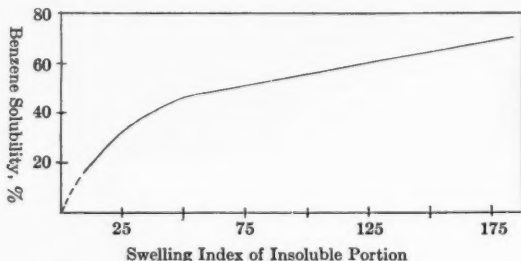


FIG. 8.—Relation of swelling indices to benzene solubilities for 75 butadiene-25 styrene rubber.

portions of highly insoluble rubbers are less swollen than the insoluble fractions of rubbers which are almost completely benzene soluble. The correlation of these values of swelling indices and benzene solubilities has been close enough so that the swelling index is no longer measured.

**Viscosity Measurements and Calculated Average Molecular Weights.**—Viscosity measurements were made of the benzene-soluble portions of butadiene-styrene polymers in an attempt to determine average molecular weights of the rubbers. The determinations were made in dilute benzene solution (0.1 to 0.3 gram per 100 cc.) in an Ostwald capillary viscometer at 25° C. The exact concentration of the solution was determined after the viscosity measurements. The preliminary tests showed considerable deviation from linearity of  $\eta_{sp}$  plotted against concentration. It was found, however, that excellent linearity is obtained by plotting  $\log_{10} \eta_R$  against concentration. This correlation was

pointed out for a large number of polymers by Kemp and Peters<sup>17</sup>. This relation permits the calculation of average molecular weights, if a satisfactory constant is determined by comparison with osmotic pressure measurements or freezing point determinations. Since osmotic pressure determinations have not yet been made for our samples, we prefer to report our results in terms of intrinsic viscosity,  $[\eta]$ , defined as the natural logarithm of the relative viscosity divided by concentration. In cases where we have used calculated average molecular weights based on viscosity measurements, we have arbitrarily adopted the constant use by Kemp and Peters, who calculated weight average molecular weights from viscosity data for rubber, Neoprene, and Buna-85 as follows:

$$\text{mol. wt.} = \frac{\log_{10} \eta_R}{C} \times 0.75 \times 10^4$$

where  $C$  is expressed in unit moles per liter. Their constant was based on cryoscopic measurements for various fractions of natural rubber. Although its use for the synthetics is not rigidly justified, the values used in our work serve the purpose of expressing relative molecular weights. Calculated on this basis, the average molecular weights for completely benzene-soluble butadiene-styrene rubber of good quality are in the range 40,000 to 50,000.

A sample of completely benzene-soluble butadiene-styrene (75-25) made in our pilot plant was checked by viscosity measurements and then submitted to the laboratories of E. I. du Pont de Nemours & Company, Inc., for ultracentrifuge tests. Through the courtesy of Cole Coolidge, G. D. Patterson, E. D. Bailey, and J. B. Nichols, molecular-weight distribution and average molecular weights were obtained.

The average molecular weight for this sample by the ultracentrifuge was 92,500. This value is approximately twice that calculated from relative viscosity determinations, using the formula and constant referred to above. This value was 44,000. Until a check against osmotic pressure measurements is available, no absolute value is attached to the molecular weights calculated from viscosity values. Since the Staudinger relation applies only to linear molecules, its application to a polymer which may be considerably branched would be expected to give low calculated molecular weights.

*Molecular Weight Distribution.*—The molecular weight distribution obtained at the du Pont laboratories by ultracentrifuging a chloroform solution of butadiene-styrene rubber is shown in Figures 9 and 10. This particular sample is somewhat richer in extremely low-molecular-weight material than the other butadiene-styrene rubbers tested.

Before the ultracentrifuge data had been obtained, our laboratory had investigated available methods of obtaining approximate molecular weight distributions. Our object was not to obtain precise distribution curves, but to develop a rapid convenient procedure which would permit a study of the changes in relative amounts of low-, intermediate-, and high-viscosity fractions with change of polymerization conditions and of mechanical treatment of the rubber.

The following method was adopted. A sample was extracted (by the same method described for benzene solubilities) with a poor solvent, and the amount and relative viscosity of the extracted polymer were determined. This extraction was then repeated on the undissolved polymer, using progressively richer blends of the poor solvent with a good solvent. The solvents for the butadiene-

styrene polymers were petroleum ether (30–60° C) and benzene. As Table I shows, it is sometimes necessary to use alcohol-petroleum ether blends for the first fractions if the sample is especially rich in low-molecular-weight polymer. The data for polymer A in Table I and Figure 11 indicate the results of our fractionation of a portion of the batch from which the sample submitted to

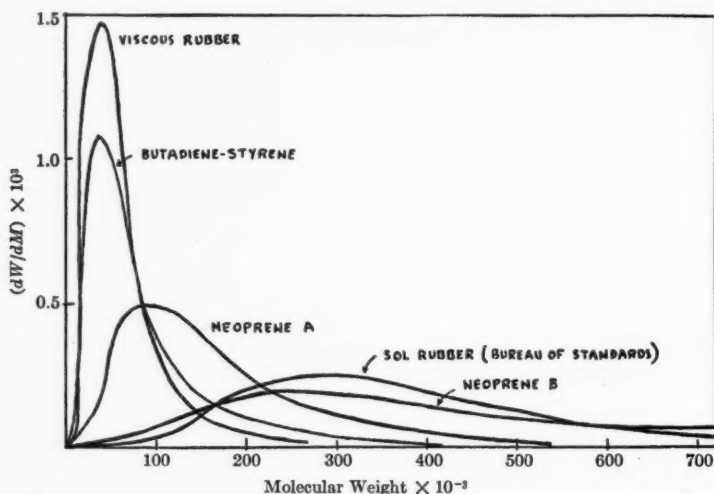


Fig. 9.—Molecular weight distributions of natural and synthetic rubbers.

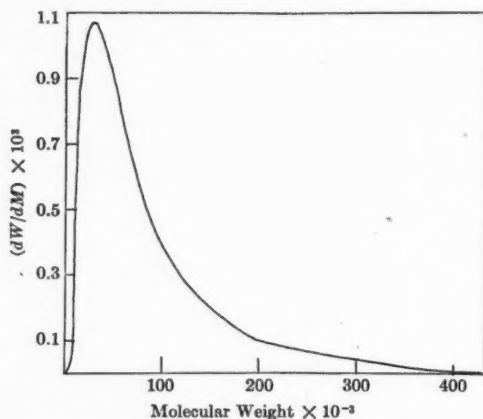


Fig. 10.—Molecular weight distribution of butadiene-styrene polymer.

du Pont was taken. Similar fractional extraction data are shown for other butadiene-styrene rubber samples to indicate the different types of distribution obtained.

In the cases where high-viscosity fractions were found, no fraction of intermediate average viscosity was found. These data do not indicate that the intermediate material was absent, but that the solvent blends, sufficiently rich in benzene to dissolve the intermediate portion, also extracted the very



Table I  
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highest. That is, the sensitivity of the fractionation is less than in the low-molecular-weight range. Since this method of fractionation gives cuts which are still quite heterogeneous, the data are to be used only for comparative

TABLE I  
SUCCESSIVE FRACTIONAL EXTRACTIONS OF BUTADIENE-STYRENE POLYMERS

Polymer	Solvent Blend <sup>a</sup> , Vol.-%	% of total rubber hydrocarbon	Intrinsic viscosity	Calcd. viscosity mol. wt.
A (9% nonrubber)	80/20 P. E./EtOH	5.1	0.33	6,500
	100	15.2	0.46	9,000
	95/5 P. E./benzene	26.3	0.92	18,000
	93/7 P. E./benzene	13.0	1.53	30,000
	91/9 P. E./benzene	24.4	3.92	77,000
	90/10 P. E./benzene	14.6	4.85	95,000
B (6% nonrubber), 50% insoluble	100 P. E.	7.8	0.42	8,000
	95/5 P. E./benzene	10.8	0.56	11,000
	91/9 P. E./benzene	16.1	1.23	24,000
	89/11 P. E./benzene	9.9	1.75	34,000
	86/14 P. E./benzene	5.0	3.74	73,500
C (9% nonrubber)	100 P. E.	7.7	0.49	9,500
	95/5 P. E./benzene	9.6	0.52	10,000
	91/9 P. E./benzene	29.3	1.28	25,000
	89/11 P. E./benzene	11.1	2.47	48,000
	86.5/13.5 P. E./benzene	29.5	6.05	118,500
	38/62 P. E./benzene	12.0	6.24	122,000

<sup>a</sup> P. E. = Petroleum ether.

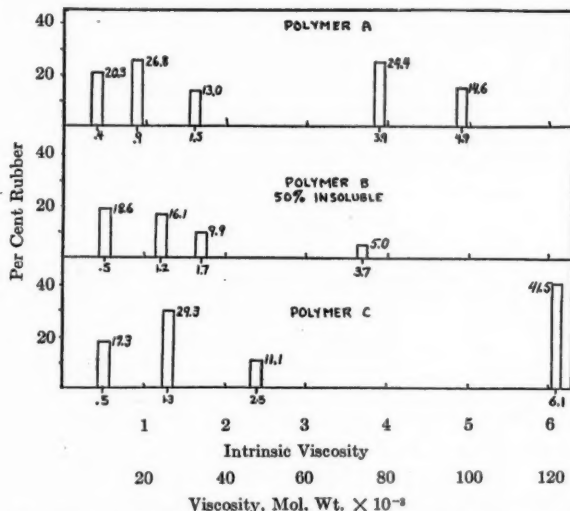


Fig. 11.—Results of fractional extraction of butadiene-styrene rubbers.

purposes. The separation is not sufficiently precise to warrant drawing complete distribution curves.

Since the successive extraction of the polymer samples by several solvent blends is time consuming (about a week for each complete determination), a

rapid method has been tested by which a fractionation is completed in less than 24 hours. It had been observed that the viscosities of the fractions of butadiene-styrene rubbers were additive, and that good agreement was found between the intrinsic viscosity (or calculated molecular weight) calculated from the amount and viscosity of the separate fractions, and the value obtained by a viscosity determination of the solution of the entire unfractionated rubber. This relation suggested fractional extraction by the following method. Several duplicate samples of the rubber were extracted for 16 hours with a series of petroleum ether-benzene blends of the compositions used in successive extractions. The amount and viscosity of the rubber extracted by each blend was determined, and the amounts and viscosities of the individual fractions calculated from those of the combined fractions were actually measured. For our purposes the agreement between this "simultaneous" extraction and the more valid "successive" extraction was highly satisfactory. The agreement is shown in Table II in which the various fractions are combined as shown.

TABLE II  
COMPARISON OF SUCCESSIVE AND SIMULTANEOUS METHODS OF FRACTIONAL EXTRACTION OF BUTADIENE-STYRENE POLYMERS

Calculated viscosity mol. wt.	% of Total rubber hydrocarbon	
	Successive method	Simultaneous method
< 12,000	20.3	17.2
12,000-30,000	26.8	30.8
30,000-60,000	13.0	15.9
60,000-85,000	24.4	24.6
> 85,000	14.6	10.9

*Effect of Milling on Solubility and Viscosity Molecular Weight.*—The tests of solubility and viscosity must be made on a sample of known history in regard to the amount of mechanical working the sample has received. Table III shows the effect of milling on the benzene solubility and viscosity of butadiene-styrene rubbers of varying solubilities in the unmilled condition.

TABLE III  
EFFECT OF MILLING ON BENZENE SOLUBILITY AND CALCULATED VISCOSITY MOLECULAR WEIGHT OF BUTADIENE-STYRENE POLYMERS

Sample	No treatment		Milled 5 minutes on tight-set 6-in. laboratory mill at 80° F	
	% soluble in benzene	Calculated viscosity molecular weight of solvable portion	% soluble in benzene	Calculated viscosity molecular weight
A	100	50,000	100	37,000
B	100	47,000	100	39,000
C	67	20,000	100	31,000
D	55	20,000	100	39,000
E	59	19,000	100	38,000
F	37	19,000	100	32,000
G	31	15,000	100	27,000
H	43	14,000	100	29,000
I	20	....	100	25,000 <sup>a</sup>

<sup>a</sup> Required 15 minutes to solubilize



All samples tested could be milled to complete solubility, but the viscosity of the rubber after milling to complete solubility was lowest for polymers of low original solubility. The viscosity of rubbers originally 100 per cent soluble was likewise lowered by milling. Since any application of the rubber must involve milling of the crumb or massed sheet polymer, our test measured solubility before and after standardized milling and the viscosity after milling.

*Interpretation of Tests.*—It has recently been pointed out by W. O. Baker of the Bell Telephone Laboratories that the described method of determining polymer solubilities (which has been used in several laboratories) may include as "benzene soluble" the polymer which is colloiddally and not molecularly dispersed. Regardless of the exact nature of the solutions obtained, the methods described have been useful in the evaluation of the effect of polymerization variables on the quality of the rubber produced. They have been applied to the study of reaction temperature, catalyst, and modifier concentration, polymer yield, emulsifier type, and other variables of the reaction.

#### ELECTRICAL PROPERTIES OF SYNTHETIC RUBBER

The electrical properties of synthetic rubbers can be fairly well anticipated from their chemical constitution and the known principles and theories of dielectrics<sup>18</sup>. In general, hydrocarbons show low dielectric constants and losses, with electrical properties insensitive to temperature. In accordance

TABLE IV  
RESULTS OF PRACTICAL MEASUREMENTS

Type of rubber	1-Kilocycle frequency		1-Megacycle frequency	
	Dielectric constant	Power factor (%)	Dielectric constant	Power factor (%)
Natural	2.69	0.271	2.52	0.695
Butyl	2.38	0.302	2.20	...
Butadiene-styrene	2.70	0.342	2.49	1.02
Butadiene-acrylonitrile	12.65	5.73	11.0	25.9

with this, butadiene-styrene rubbers, polyisobutylene, and Butyl rubber have excellent properties as electrical insulators. Any electric power absorption observed for these uncompounded rubbers can almost certainly be attributed to traces of impurities or moisture absorption due to impurities. To this extent there is a field of application here for synthetic rubber in which it is not fundamentally at any disadvantage to natural rubber.

For compounded stocks of these hydrocarbon rubbers, the electrical properties will be almost entirely determined by the ingredients which it is found necessary to add to secure desirable physical properties. Since these hydrocarbon rubbers are so inactive electrically, at least for frequencies up to a few megacycles, electrical measurements on them require the highest degree of precision, are influenced by traces of impurities, and in this range afford little insight into the structure.

The electrical properties of butadiene-acrylonitrile rubbers are less interesting from a technical standpoint because they are so poor. They have a considerable degree of scientific interest because they can be used to study the molecular structure of the polymer with respect to the movement of segments of the chain molecules under the action of an alternating electric field.

For butadiene-acrylonitrile rubbers, there are polar groups attached to the long-chain molecules. These attempt to align themselves to an applied electric field, so that, in case of an alternating field, molecular rotations occur, and power is absorbed due to internal viscosity.

In addition to this type of power absorption, due to dipole rotation, there are undoubtedly other losses due to mechanisms such as ionic conduction, since the direct-current resistivities of the butadiene-acrylonitrile rubbers are relatively low<sup>19</sup>.

Table IV gives typical results of electrical measurements on gum stocks of natural rubber, several hydrocarbon synthetic rubbers, and a nitrile rubber. The measurements were made in the Goodyear laboratories by R. B. Stambaugh, using General Radio audio- and radiofrequency bridges.

#### COMPARISON OF SYNTHETIC RUBBERS IN VIBRATION

In a paper from our research laboratories, given before the Society of Automotive Engineers in Detroit in 1941, a method of determining the hysteresis and internal friction of rubber stocks was described. The application of this method to synthetic rubber has been extended to give the comparison between

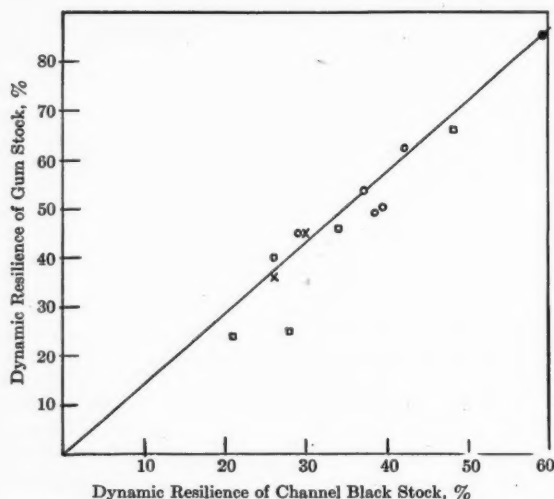


Fig. 12.—Relation in dynamic resilience between channel black and gum stocks.

Starting Ratio for Polymer	
□	Butadiene 50
○	Butadiene 70
×	Butadiene 75
●	Natural Rubber
	Acrylonitrile 50
	Styrene 30
	25

natural rubber and the synthetic rubbers which are under discussion in this paper. The measurement of synthetic rubbers when subjected to a vibratory driving force of known magnitude offers a convenient and accurate method of evaluating the stiffness and resilience for small deformations such as occur in many important applications. The technique has been described<sup>20</sup>.

Although general practice in testing the physical properties of synthetic rubber is to use a test formula containing gas black, it seemed worthwhile to

determine whether vibration measurements on gum stocks might not give a more fundamental comparison of the elastic properties of the polymer itself. By systematic variation of the conditions during polymerization, a series of butadiene-acrylonitrile rubbers was prepared which showed a wide range in dynamic resilience. These were tested when compounded as gum stocks and as tread stocks. The results are shown in Figure 12. There is an essentially linear correlation between the resilience of the tread stocks and the gum stocks. The straight line shown was drawn between the origin and the point for natural rubber. The points, especially those of the 70/30 nitrile polymers and the two styrene polymers, fall so near the straight line that for most purposes it can

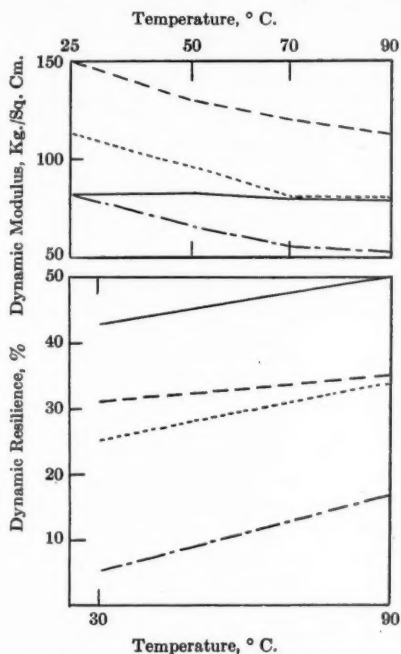


FIG. 13.—Effect of temperature on dynamic modulus and dynamic resilience of various channel black stocks.

— Natural rubber      - - - Buta-S  
 - - - Buta-N      - · - Butyl

be assumed that the relative values of the gum stocks persist after the addition of gas black. Furthermore, it can be inferred that carbon black reinforcement affects the resilience of both natural and synthetic rubbers in the same way and by essentially the same mechanism. The general rule appears to be that 40 parts of gas black in 100 parts of polymer cause a 40 per cent decrease in the resilience from the value for the gum stock.

It is advantageous in comparing the properties of various synthetic rubbers to include measurements over a range of temperature since, in many cases, the properties change much more rapidly with temperature in the operating range than do those of natural rubber.

Figure 13 shows the dynamic modulus of tread stocks of natural, Butyl, butadiene-styrene, and butadiene-acrylonitrile rubbers as a function of the

temperature for a range from room temperature to 90° C. The effect of temperature in this range on the dynamic modulus of natural rubber is much less than for the other rubbers. At lower temperatures the dynamic modulus for natural rubber would also begin to show a large temperature dependence. The curves illustrate a fundamental difference between these synthetic rubbers and natural rubber which can be expressed by saying that the temperature range in which they exhibit rubberlike properties is shorter than for natural rubber and is shifted to higher temperature. There are some reasons for supposing that this is analogous to the difference between rubber and gutta-percha, and is related to an essentially *trans* form of the chain molecules for synthetic rubbers, compared to the *cis* form for natural rubber.

Figure 13 shows the dynamic resilience of the same tread stock *vs.* temperature. The superior resilience of natural rubber is plainly shown. The nitrile and styrene rubbers had about the same resilience, which was considerably lower than for natural rubber. The Butyl rubber stock was lower still.

TABLE V  
COMPARISON OF SYNTHETIC RUBBERS IN FLEXOMETER TEST  
(STATIC COMPRESSION, 6 PER CENT)

Type of rubber	Temperature rise (° C) at amplitude of	
	1/16 inch	3/32 inch
Natural	49.5	70.5
Butyl	78.5	102.5
Butadiene-acrylonitrile	77.0	96.0
Butadiene-styrene	71.5	90.5

Measurements were made by a thermocouple of the temperature rise in the center of 1 × 1 × 2 inch blocks of these stocks when subjected to 60-cycle-per-second vibrations of fixed amplitude in the lengthwise direction, using a large flexometer operating on the same principle as the small vibrator employed for the previous measurements. The results are shown in Table V. Again, the superiority of natural rubber is plainly evident. The lower dynamic modulus of Butyl rubber helps counteract the effect of its low resilience in this test so that the observed temperature rise is not so much greater than for the other synthetic rubbers.

#### CHEMICAL UNSATURATION

Cheyney and Kelley<sup>21</sup> have set forth their findings regarding chemical unsaturation. Briefly, they found that the unsaturation, measured by the iodine chloride method, gave approximately 90 per cent of the amount which would be expected of a straight lineal copolymer, rubber being considered as 100 per cent on the same basis.

#### PRACTICAL ASPECTS

Turning now from the purely scientific aspects of the synthetic rubber problem to the more practical aspects of commercial utilization of the various types of synthetic rubbers, the comparative physical properties in a standard series of formulas will be discussed.

Formulas for the three synthetic rubbers compared with natural rubber are given in Table VI, both for compounds containing no carbon black and

for those containing substantial amounts of black. We do not contend that these formulas represent the maximum properties to be obtained with the synthetic rubbers, since there may be various opinions as to what constitutes the best type of compounding. However, it is believed that the results outlined

TABLE VI  
FORMULAS FOR GUM AND TREAD COMPOUNDS

	Natural	Buta-N	Buta-S	Butyl
<b>Gum compounds</b>				
Smoked sheet	100.0	....	....	....
Buna-N	....	100.0	....	....
Buna-S	....	....	100.0	....
Butyl-B	....	....	....	100.0
Mercaptobenzothiazole	0.5	1.0	1.0	....
Tetramethylthiuram disulfide	....	....	....	1.0
Sulfur	3.0	2.0	2.0	1.5 <sup>a</sup>
Zinc oxide	5.0	5.0	5.0	5.0 <sup>a</sup>
Stearic acid	1.0	1.0	1.0	3.0
Phenyl- $\alpha$ -naphthylamine	....	1.5 <sup>a</sup>	1.5 <sup>a</sup>	....
Phenyl- $\beta$ -naphthylamine	....	1.5 <sup>a</sup>	1.5 <sup>a</sup>	....
	109.5	112.0	112.0	110.5
<b>Tread compounds</b>				
Smoked sheet	100.0	....	....	....
Buna-N	....	100.0	....	....
Buna-S	....	....	100.0	....
Butyl-B	....	....	....	100.0
Mercaptobenzothiazole	1.25	1.5	1.5	....
Tetramethylthiuram disulfide	....	....	....	1.0
Sulfur	3.0	2.0	2.0	1.5 <sup>a</sup>
Zinc oxide	5.0	5.0	5.0	5.0 <sup>a</sup>
Channel black	50.0	50.0	50.0	60.0
Stearic acid	3.0	2.0	2.0	3.0
Phenyl- $\alpha$ -naphthylamine	....	1.5 <sup>a</sup>	1.5 <sup>a</sup>	....
Phenyl- $\beta$ -naphthylamine	1.0	1.5 <sup>a</sup>	1.5 <sup>a</sup>	....
Pine tar	3.0	....	....	....
Barrett No. 10	....	3.0	3.0	....
Medium process oil	....	....	....	3.0
	166.25	166.5	166.5	173.5

<sup>a</sup> Included in the polymer.

in the succeeding pages are substantially representative of the general properties of the rubbers under consideration.

#### PROPERTIES OF GUM COMPOUNDS

Figure 14 represents the effect of milling on the plasticity and recovery of the various rubbers. Two determinations were made: original, after one pass through a tight cold mill; milled, after ten passes through the same mill. While the original plasticity-recovery data show but little difference between the rubbers, the milled data show that the natural rubber becomes much more plasticized than the synthetics. The latter give plasticities of the same order under this treatment; all are considerably stiffer than natural rubber. It should be noted that, while the drop in plasticity between one and ten passes is about 75 per cent for natural rubber, there is only a 10 per cent decrease for the synthetics.

Figure 15 represents the effect of the same type of milling on the extrusion of the rubbers. The synthetics have high original extrusion values, but milling changes completely the picture and shows that natural rubber undergoes a considerable breakdown, while there is only a slight effect on the synthetics.

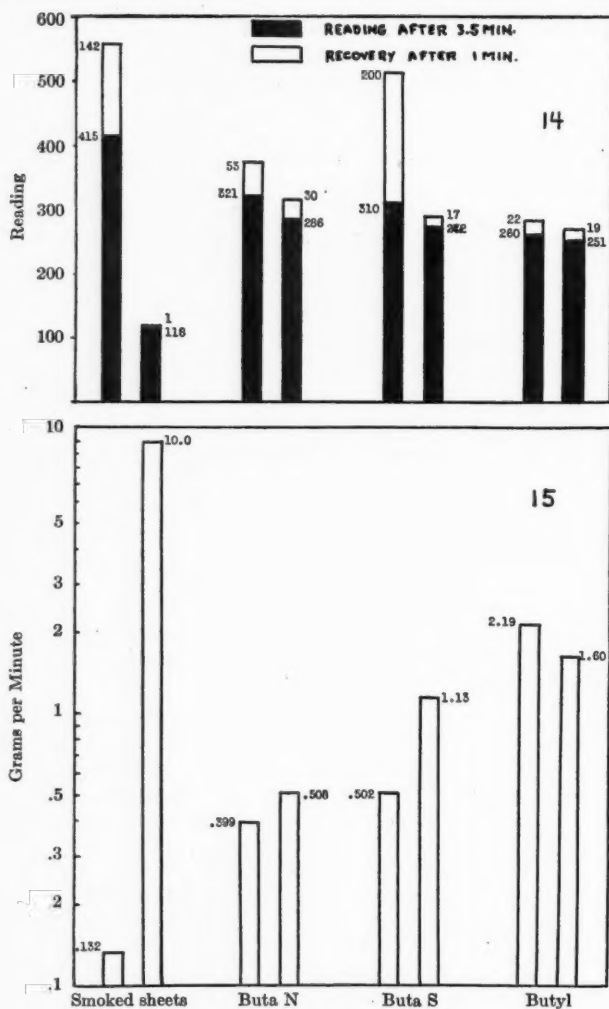
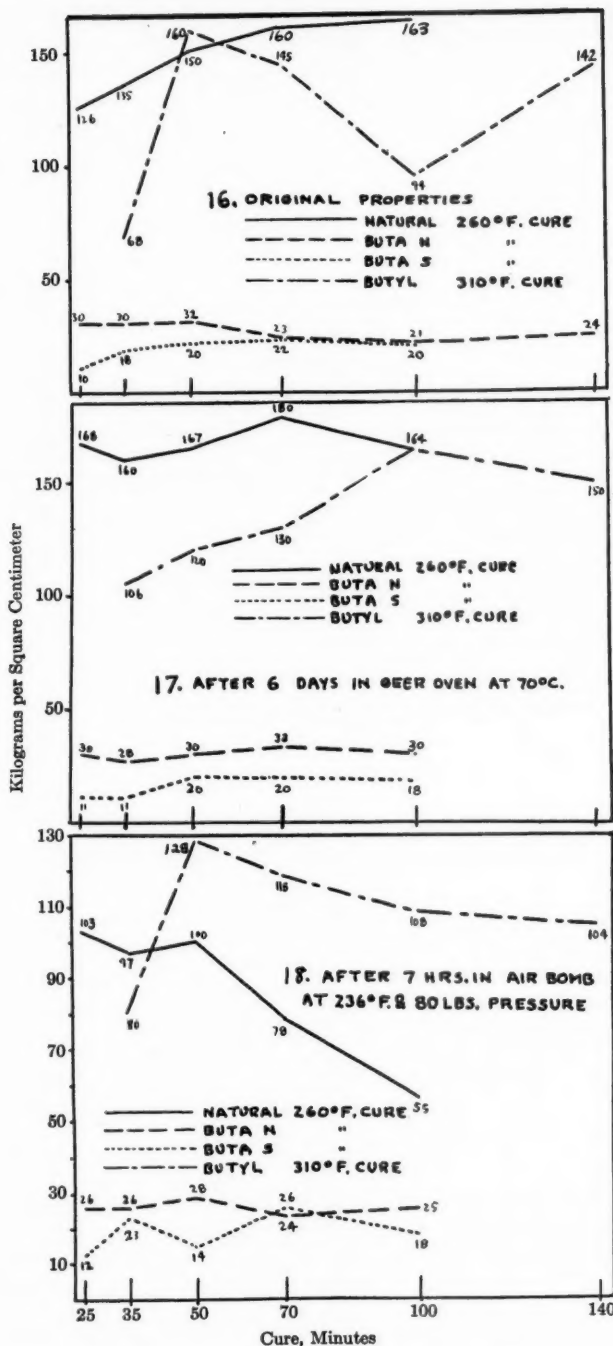


FIG. 14.—Effect of milling on plasticity and recovery of various rubbers (10 kg. weight, 70° C, 15-minute preheat).

FIG. 15.—Effect of milling on extrusion characteristics of various rubbers at 200 pounds per square inch and 92° C.  
Left-hand bar of each pair, original; right-hand bar, milled.

The tensile characteristics of the four rubbers, compounded in a pure-gum stock, are shown in Figure 16. Cures at 260° F were run on all compounds except the Butyl, in which case 310° F was required to bring out the best physical characteristics. It is well known that butadiene copolymers do not



FIGS. 16 TO 18.—Tensile characteristics of gum stocks.



develop their best properties in pure-gum compounds, whereas Butyl does not compare too unfavorably with natural rubber. Figure 16 shows natural rubber to be far superior to the synthetics. Butadiene-acrylonitrile and butadiene-styrene are of low quality; the Butyl rubber is about halfway between the two. The curing curve for butadiene-acrylonitrile, butadiene-

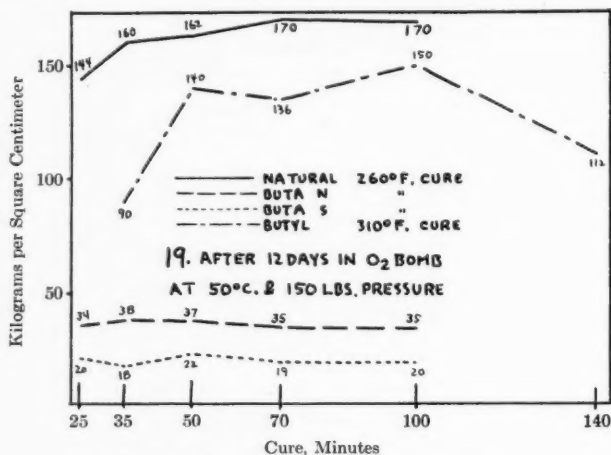


FIG. 19.—Tensile characteristics of gum stocks.

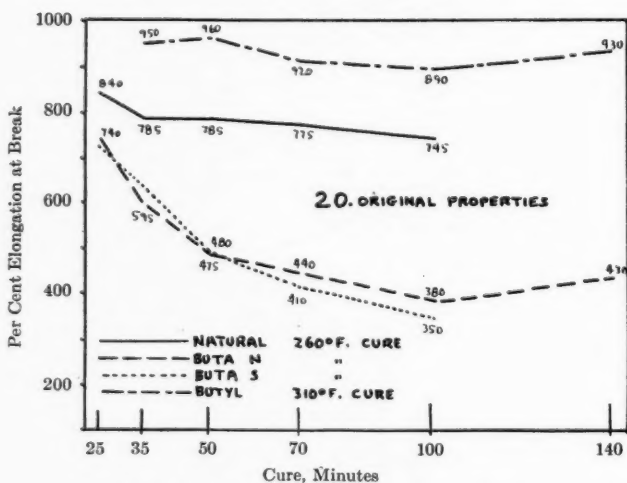


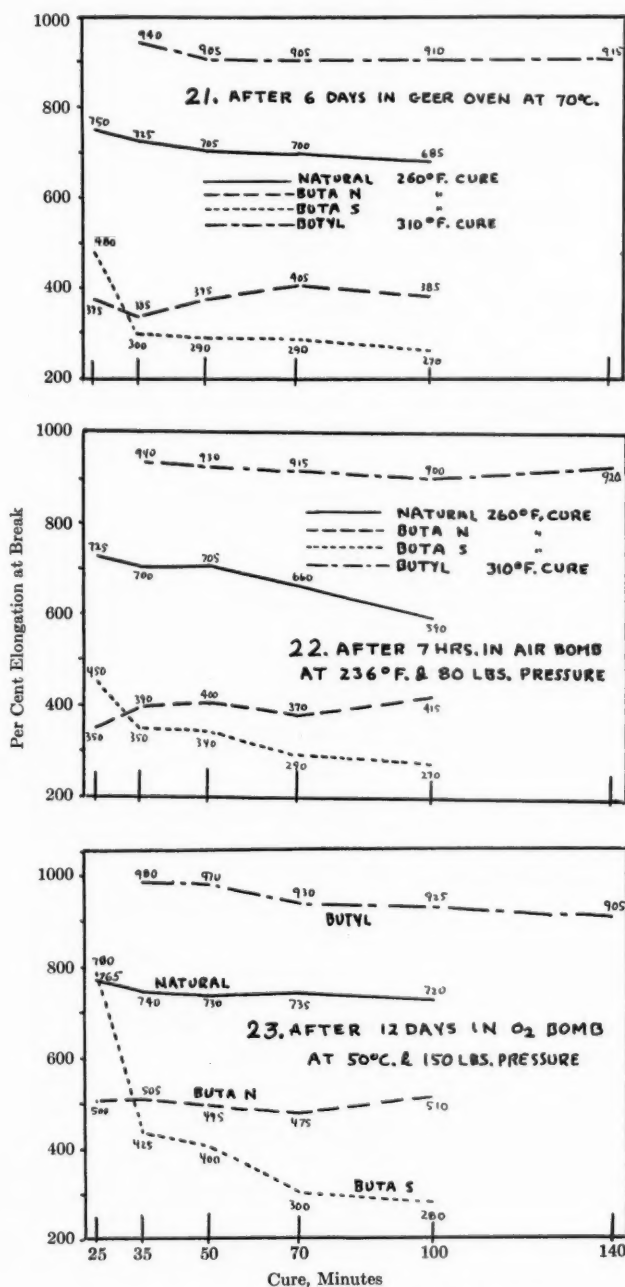
FIG. 20.—Elongation characteristics of gum stocks.

styrene and natural rubber is flat; Butyl rubber is comparatively slow curing; in fact it required 50 minutes to reach its optimum.

Figure 17 presents the tensile characteristics after aging for 6 days at 70° C. All compounds age equally well under these conditions; there is little change from the original properties.

Figure 18 shows the properties after aging in an air bomb for 7 hours at 236° F and 80 pounds air pressure. This test brings out the heat-resistant





FIGS. 21 to 23.—Elongation characteristics of gum stocks.

properties of the synthetics. Comparison of this chart with the data presented in Figure 16 shows that natural rubber falls off decidedly after the 50-minute cure. The properties of Butyl rubber improve rather than decrease, while the

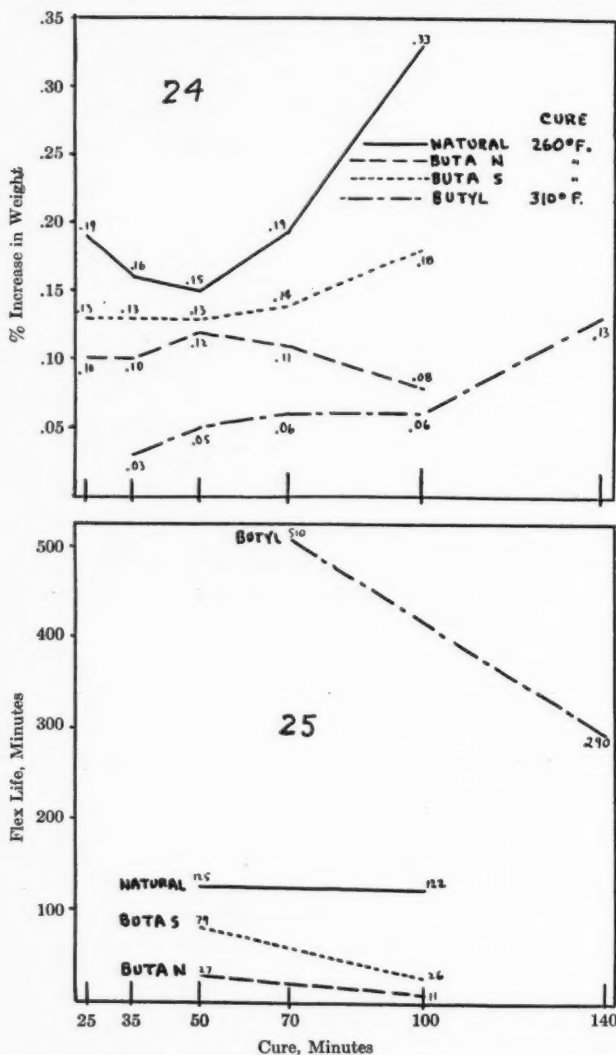
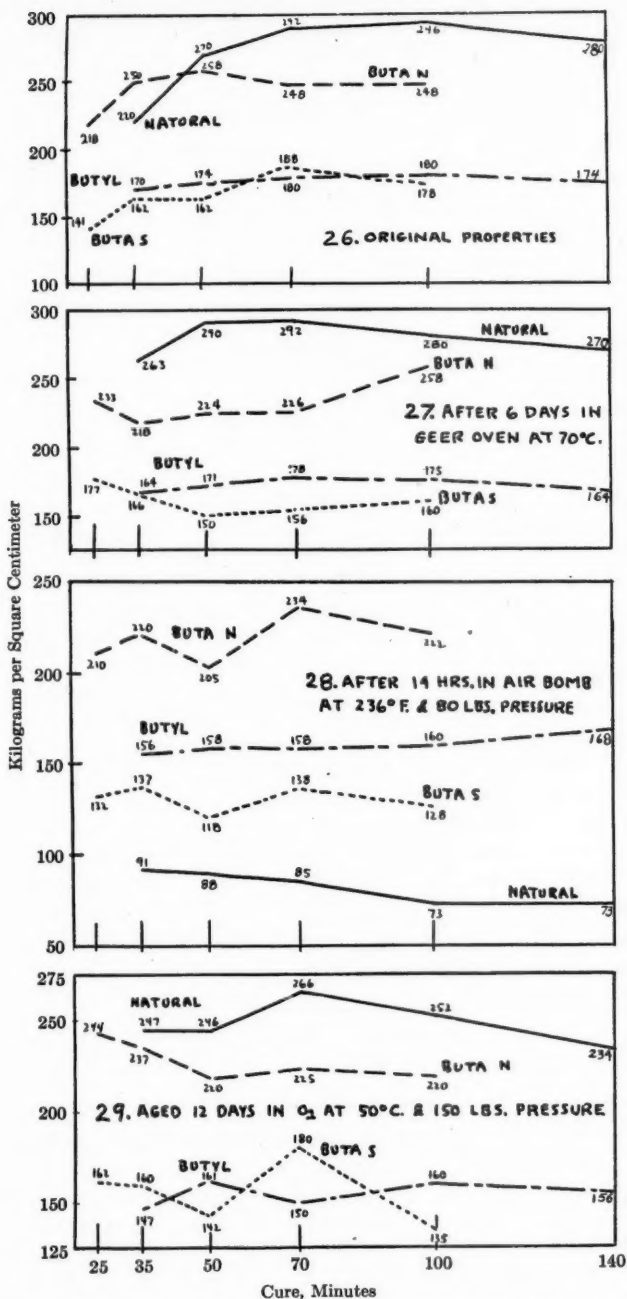


FIG. 24.—Weight increase of gum stocks after 12 days in oxygen bomb at 50° C and 150 pounds pressure.

FIG. 25.—Flex life characteristics of gum stocks stretched 0-116 per cent at 370 cycles per minute.

acrylonitrile- and styrene-butadienes also increase slightly and do not fall off over the range.

Figure 19 presents the tensile data after 12 days in the oxygen bomb at 50° C and 150 pounds pressure. As in the Geer oven test, there is practically no change over the original properties.



FIGS. 26 TO 29.—Tensile characteristics of channel black stocks.

Natural	260° F cure	50 parts loading
Buta-N	260° F	50 parts
Buta-S	290° F	50 parts
Butyl	310° F	60 parts

The elongation characteristics of the pure gum compounds, before and after various aging tests are given in Figures 20 to 23. Figure 20 shows that the original elongations of Butyl rubber are highest, closely followed by natural rubber; the acrylonitrile and styrene rubbers are considerably lower, especially on the higher cures.

After 6 days at 70° C in the Geer oven (Figure 21) there is no change in the elongations of natural and Butyl rubbers; butadiene-acrylonitrile and butadiene-styrene show a considerable decrease on the low cures, but level off to their original figures after 35 minutes.

Results after 7 hours in the air bomb at 236° F and 80 pounds air pressure (Figure 22) are of the same order as for the Geer-oven data. Butyl and natural rubber are relatively unaffected, but there is a drop on the low cures of butadiene-acrylonitrile and butadiene-styrene.

Figure 23 represents the effect of 12 days in the oxygen bomb at 50° C and 150 pounds pressure on these compounds. There is no change in natural, Butyl, and butadiene-styrene rubbers from the originals, whereas butadiene-acrylonitrile shows an increase in elongation on the high cures.

Figure 24 represents the weight increase by the four gum stocks after 12 days in the oxygen bomb at 50° C and 150 pounds pressure. Natural rubber absorbs considerably more weight, due to oxidation under the conditions of test, than any of the synthetics. Of the latter, Butyl rubber is least affected.

Figure 25 shows the relative flexing of the natural and synthetic rubbers in a pure-gum stock. The standard punched-hole flexing test was used. This was run at 0-116 per cent stretch at the rate of 370 cycles per minute. Although falling off considerably over the range, Butyl rubber is still outstanding compared to the others of this group. Natural rubber is superior to the butadiene-acrylonitrile and butadiene-styrene, both of which give poor results.

#### PROPERTIES OF TREAD COMPOUNDS

Thus far we have considered the rubbers in pure gum compounds (that is, without loading). The following data show the effects of channel black loading on the rubbers. Original data for channel black loaded stocks are presented in Figure 26. Butyl and butadiene-styrene are of the same order, and give lower results than butadiene-acrylonitrile and natural rubber, the latter of which is slightly higher. All compounds have approximately the same rate of cure and, after the optimum is reached, remain flat-curing over the range.

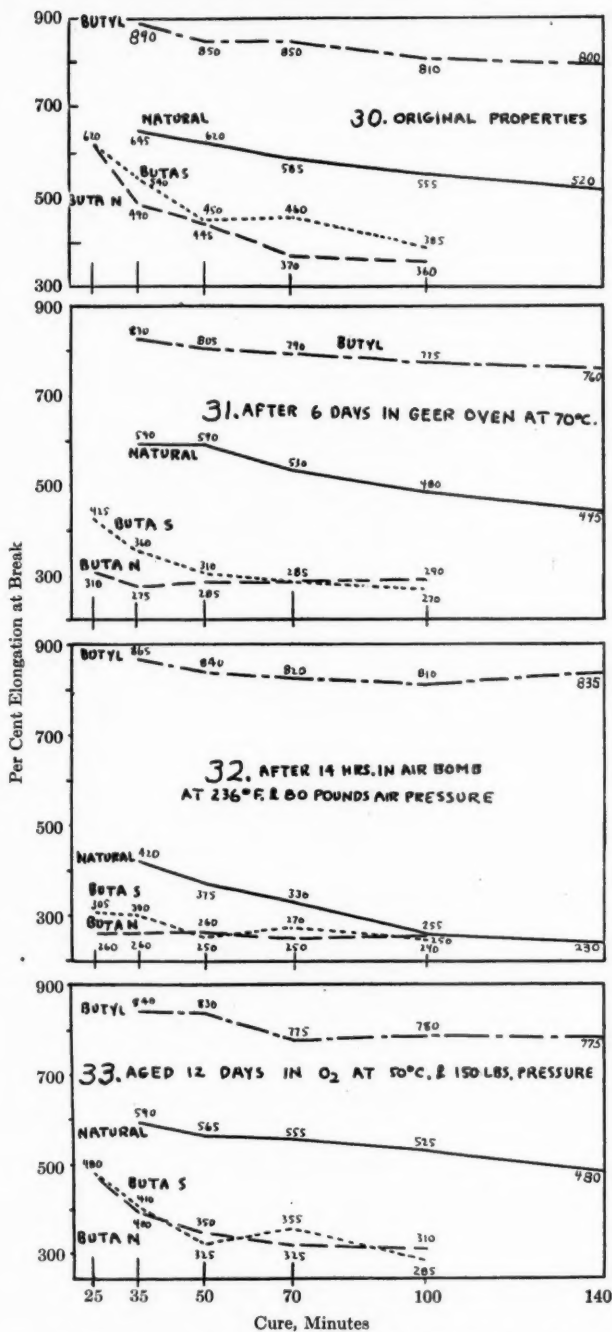
Comparison of Figures 26 and 16 illustrates the effect of channel black in these synthetics. Butadiene-acrylonitrile and butadiene-styrene and Butyl rubber show large increases in tensile strength, and the Butyl rubber range of cures is smoothed out. There is some increase in the tensile of natural rubber, but it is not nearly so great as for the synthetics.

Tensile aging data for the channel black loadings are presented on Figures 27, 28, and 29. Figure 27 represents the Geer oven aging for 6 days at 70° C. It shows no great change for any of the rubbers over the originals.

Figure 28 presents data on air-bomb aging, run for 14 hours at 236° F and 80 pounds pressure. Natural rubber has decreased considerably over the originals, while Butyl rubber and butadiene-acrylonitrile show increases. Butadiene-styrene is unchanged.

All the rubbers decrease correspondingly in tensile after 12 days in the oxygen bomb at 50° C and 150 pounds pressure (Figure 29).

Original and aging characteristics of the elongations on the channel black loadings are given in Figures 30 to 33. The original data on Figure 30 show



Figs. 30 to 33.—Elongation characteristics of channel black stocks.

Natural	260° F cure	50 parts loading
Buta-N	260° F	50 parts
Buta-S	290° F	50 parts
Butyl	310° F	60 parts

Butyl rubber to have the highest elongation, followed by natural rubber. Both of them are comparatively flat over the range. Butadiene-acrylonitrile and butadiene-styrene are of the same order and are the lowest of this series. There is a drop in their elongations after 25 minutes, after which they remain flat through 100 minutes.

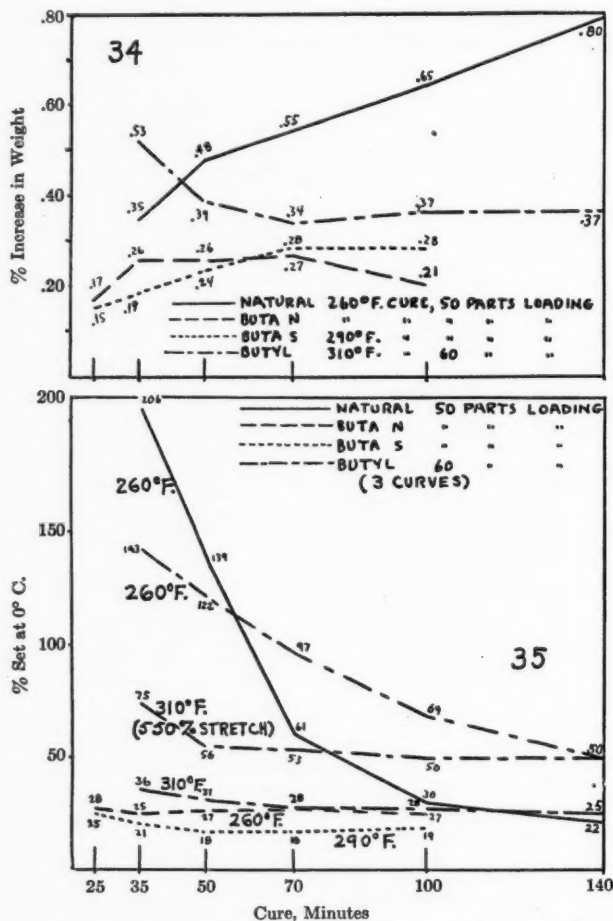


FIG. 34.—Weight increase in channel black stocks after 12 days in oxygen at 50° C and 150 pounds pressure.

FIG. 35.—Zero set in channel black stocks at 300 per cent initial stretch (cures in °F on each curve).

Natural and Butyl rubbers are unaffected by the 6-day Geer oven test (Figure 31), but there is a drop from the original data for butadiene-acrylonitrile and butadiene-styrene.

Natural rubber shows a decided decrease in elongation after 14 hours in the air bomb at 236° F and 80 pounds pressure (Figure 32). Butadiene-acrylonitrile and butadiene-styrene also decrease, but not so much; Butyl rubber is unchanged.



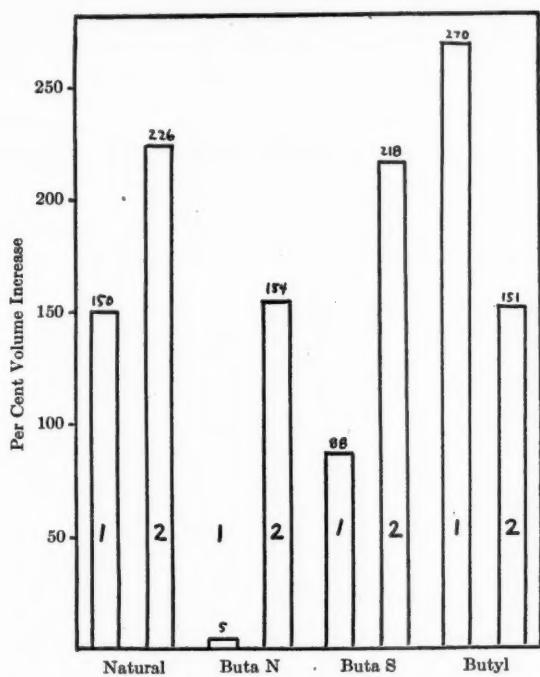


FIG. 36.—Volume increase of channel black stocks after 7-day swelling in (1) 100-octane gas and (2) benzene.

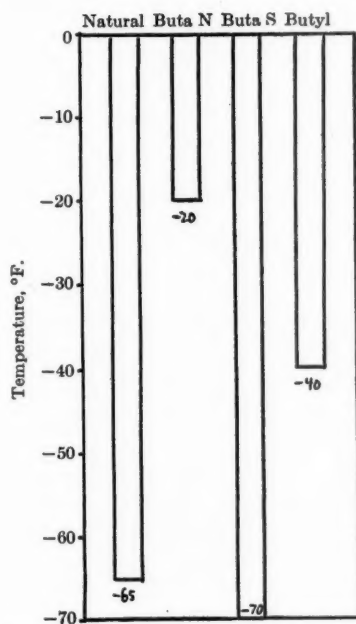
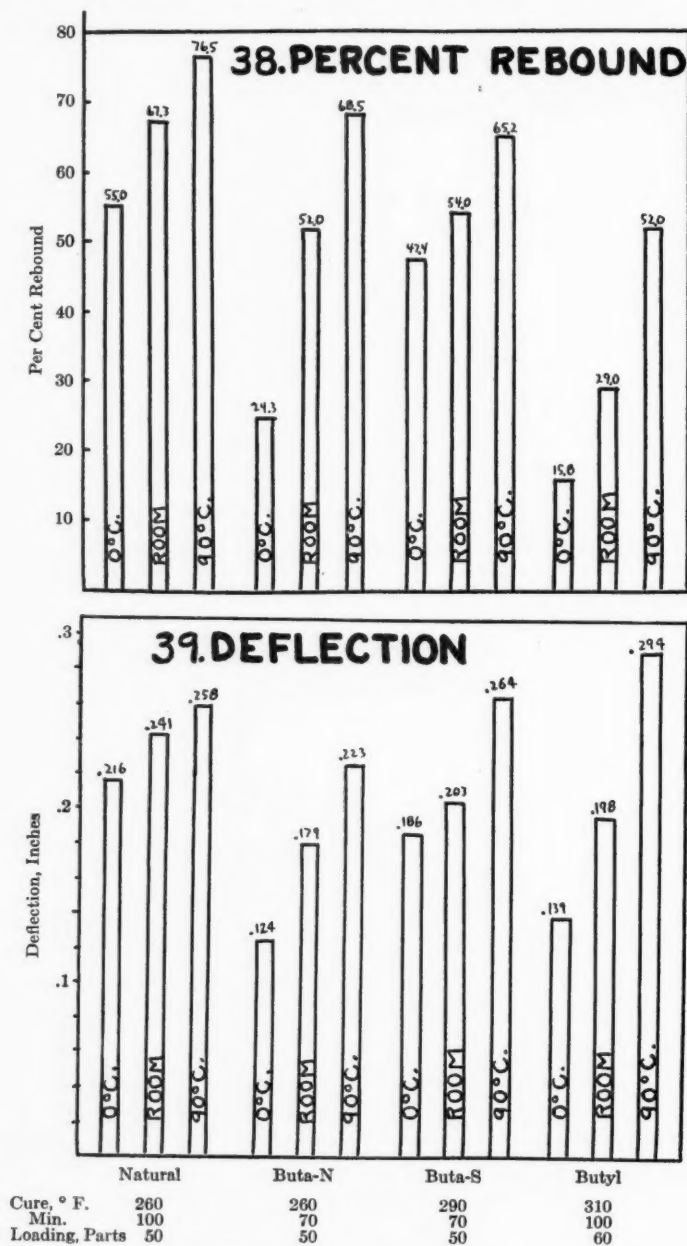


FIG. 37.—Brittle point of channel black stocks.

Figure 33 shows the elongations after 12 days in the oxygen bomb at 50° C and 150 pounds pressure. Natural and Butyl rubbers are unaffected, whereas there is a slight decrease in acrylonitrile- and styrene-butadienes.



FIGS. 38 and 39.—Rebound and deflection of channel black stocks.

Figure 34 shows the weight increase after 12 days in the oxygen bomb of the channel-black-loaded rubbers over a range of cures. As in the case of the pure-gum stocks (Figure 24), natural rubber picks up considerably more weight, due to oxidation than the synthetics. Whereas Butyl rubber was outstanding in this respect in a pure gum stock, it is now replaced by butadiene-acrylonitrile and butadiene-styrene, both of which have lower weights.

Figure 35 represents the percentage set at 0° C of the four rubbers. When properly cured, the synthetics were much less affected by this test than was natural rubber. Butyl rubber cured at 260° F gave results similar to natural rubber, but showed marked improvement when cured at 310° F.

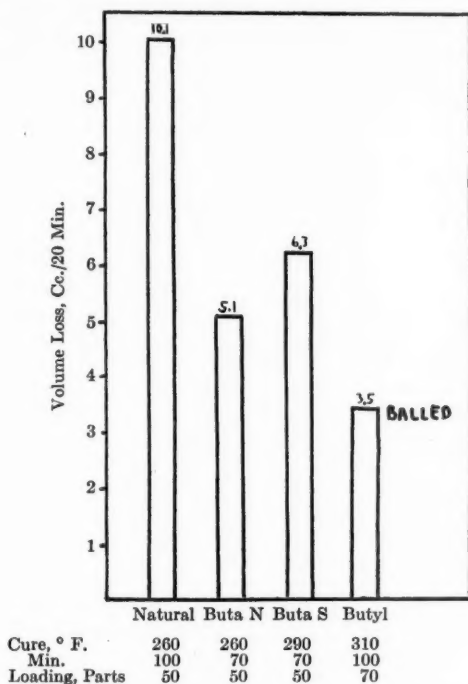
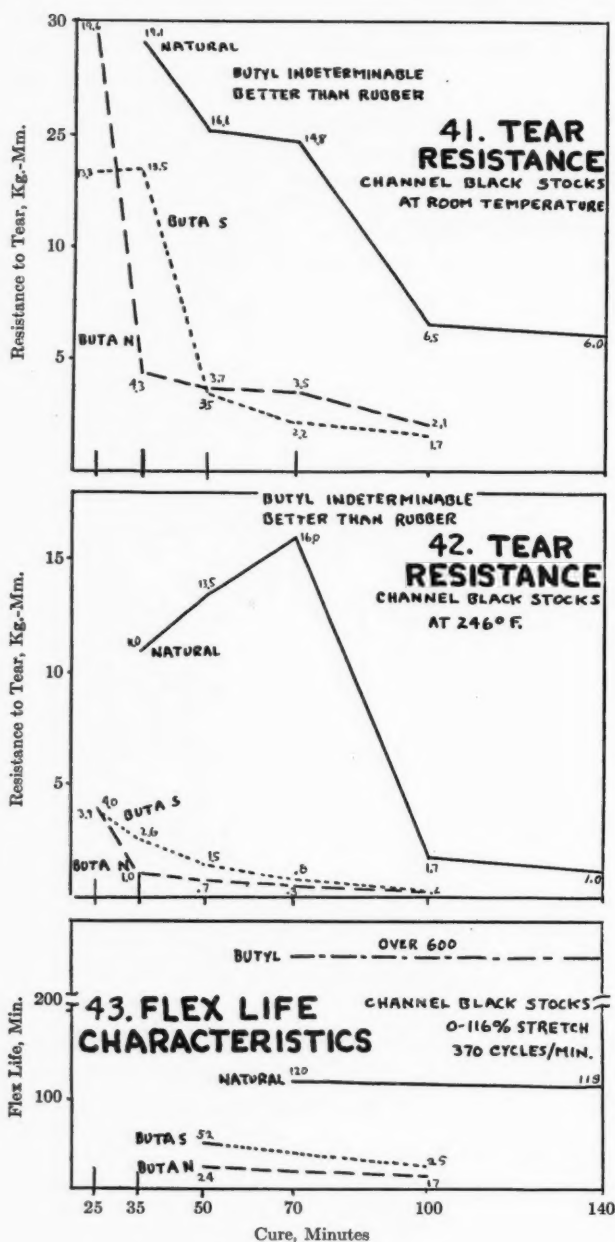


Fig. 40.—Angle abrasion of channel black stocks.

The percentage increase in volume of the channel black compounds after 7-day immersion in 100-octane gasoline and in benzene is given in Figure 36. Butyl rubber is inferior to natural rubber in 100-octane gasoline, whereas butadiene-styrene is 50 per cent better. Butadiene-acrylonitrile is the best of the synthetics. Butyl rubber is equivalent to butadiene-acrylonitrile in benzene, whereas both butadiene-styrene and natural rubber give 70 per cent higher values.

The brittle points of the four rubbers are represented in Figure 37. Butadiene-styrene is the equivalent of natural rubber from the standpoint of flexibility, whereas butadiene-acrylonitrile is much less able to withstand low temperatures. Butyl rubber falls midway between the two extremes.

Figures 38 and 39 illustrate the rebound and deflection of the channel black stocks at 0° C, room temperature, and 90° C. Natural rubber shows



FIGS. 41, 42, AND 43.

Natural	260° F cure	50 parts loading
Buta-N	260° F	50 parts
Buta-S	290° F	50 parts
Butyl	310° F	60 parts

the highest rebound values over the range, and Butyl rubber the lowest. Butadiene-acrylonitrile and butadiene-styrene give equivalent values at room temperature and at 90° C, but the styrene rubber is considerably higher at 0° C. The synthetics show more improvement in deflection as the temperature is increased than does natural rubber. This improvement is outstanding in the case of Butyl rubber. Butadiene-acrylonitrile becomes progressively higher over the range, while there is also a decided increase between room temperature and 90° C for the styrene rubber.

Figure 40 shows the effect of testing the four stocks with the angle abrasion machine. All of the synthetics are approximately twice as resistant to abrasion as the natural rubber compound.

Figures 41 and 42 illustrate the tear resistance of the channel black stocks at room temperature and at 246° F. In both cases natural rubber is superior to the acrylonitrile and styrene rubbers, and Butyl rubber is superior to natural.

Figure 43 represents the flex life of the channel black compounds, determined by standard punched-strip tests; 370 cycles per minute at 0-116 per cent

TABLE VII  
COLD vs. HOT FLEX TEST

		Flex life (minutes)		
		Natural rubber— mercaptobenzo- thiazole	GR-S	
			Mercaptobenzo- thiazole	S-2164
Room temp.	70/275° F	400	25	25
	140/275° F	400	15	35
200° F	70/275° F	600	2.3	4.0
	140/275° F	450	1.8	8.0

stretch were run. The superiority of Butyl rubber is outstanding, and natural rubber shows up much better than the acrylonitrile- or styrene-butadienes, which are very poor. The effect on the flex life of changing acceleration is important; an illustration is given in Table VII. Table VII shows the effect of flexing a natural rubber mercaptobenzothiazole stock as compared with GR-S rubber using mercaptobenzothiazole and also an accelerator of a special type. A pierced-groove test was made. This is not strictly comparable to the

TABLE VIII  
COMPARISON OF SYNTHETIC RUBBERS IN FLEXOMETER TEST  
(STATIC COMPRESSION 6 PER CENT)

Type of Rubber	Temperature rise (° C) at amplitude of	
	1/16 inch	3/32 inch
Natural	49.5	70.5
Butyl	78.5	102.5
Nitrile	77.0	96.0
Styrene	71.5	90.5

flexing test previously discussed. Here again the results are given in minutes and, although the change in accelerator made little difference at room temperature, there was a marked improvement at 200° F.

Table VIII compares synthetic and natural rubbers on a flexometer test under a static compression of 6 per cent. The temperature rise between amplitudes of 1/16 and 3/32 inch is approximately the same (20° C for each

rubber). Natural rubber has the lowest temperature for each amplitude; the synthetics are approximately 20° higher.

Synthetic rubber compounds have been known to give very low values when tested at elevated temperatures. The four stocks in question were tested at 82° and 200° F. The tensile results are shown in Figure 44. The natural

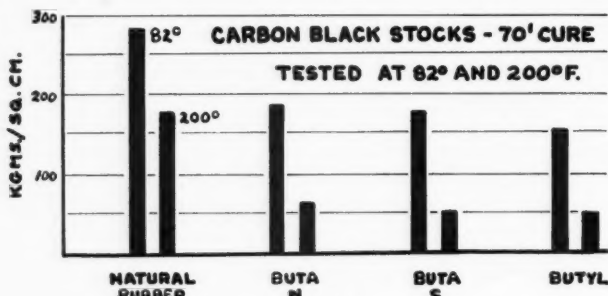


FIG. 44.—Effect of temperature on tensile strength.

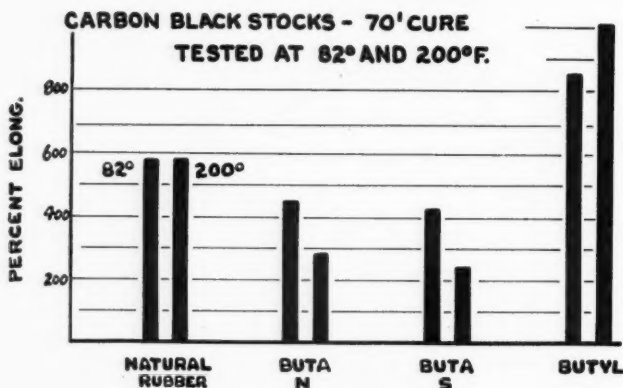


FIG. 45.—Effect of temperature on elongation.

rubber had a tensile strength of approximately 280 kg. per sq. cm. at 82° F; at 200° F it had dropped only to approximately the same level as the original tensiles of the synthetic rubbers. These, in turn, had lost tensile strength at 200° F until they were little more than 50 kg. when tested at this temperature. This is undoubtedly a serious defect in the present type of synthetic rubber which should be corrected if possible.

When tested at 82° and 200° F, the elongations (Figure 45) of natural rubber are unchanged, while the synthetics decrease approximately 150 per cent.

#### ACKNOWLEDGMENT

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# THE ELASTICITY OF A NETWORK OF LONG-CHAIN MOLECULES. I\*

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According to the kinetic theory of elasticity of rubberlike materials, originally propounded by Meyer, von Susich and Valko<sup>1</sup>, and subsequently developed by Guth and Mark<sup>2</sup> and by Kuhn<sup>3</sup>, the retractive force in stretched rubber is due to the thermal motions of the carbon atoms of the molecular chain. On the assumption of free, or effectively free, rotations about each of the C—C bonds, it is shown that, in the absence of external restraints, the molecule will take up a randomly-kinked form, in which its average length (measured by the distance between its ends) is only a small fraction of the length of the fully extended chain. The statistical treatment of the problem<sup>4</sup> leads to a formula defining the probability of a given length in terms of the molecular parameters.

An extension of the treatment to a three-dimensional network of molecules, to account for the properties of a rubber in bulk, has been attempted by various authors, notably by Kuhn<sup>3</sup> and by Wall<sup>5</sup>. Their results, however, are not in agreement. In the present paper, the methods of Kuhn and of Wall are critically examined, and the source of the discrepancies between their results is demonstrated.

## 1. WALL'S TREATMENT OF ELONGATION

In this discussion the historical order is reversed, and Wall's work is considered before that of Kuhn, which appeared eight years earlier.

Working on the basis of Kuhn's statistics of the individual molecule, Wall set out to calculate the entropy of a network of  $N_0$  equal molecules making up a cylinder of length  $l_0$  in the undeformed and  $l$  in the deformed state. For this structure, the distribution of lengths, *i.e.*, distances between junction points, of the molecules in the undeformed state was assumed to be that given by Kuhn's formula, which may be written:

$$p(x, y, z) dx \cdot dy \cdot dz = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(x^2+y^2+z^2)} dx \cdot dy \cdot dz \quad (1)$$

In this equation,  $x$ ,  $y$  and  $z$  represent the components of length of a given molecule along each of the three coördinate axes, and

$$\frac{1}{\beta^2} = \frac{2}{3} l_c^2 Z \frac{1 + \cos \theta}{1 - \cos \theta} \quad (1a)$$

$l_c$  being the C—C bond distance,  $Z$  the number of links in the molecular chain, and  $\theta$  the supplement of the valence angle. To describe the deformation, Wall assumed that the volume remains unchanged, and that the components of length of each molecule change in the same ratio as the corresponding dimensions of the bulk rubber. Thus, writing  $\alpha$  for  $l/l_0$ ,  $x$ ,  $y$  and  $z$  are changed

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to  $\alpha x$ ,  $\alpha^{-1}y$  and  $\alpha^{-1}z$  respectively<sup>6</sup>, and the corresponding distribution function is:

$$p'(x, y, z) dx \cdot dy \cdot dz = \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2[x^2/\alpha^2 + \alpha(y^2 + z^2)]} dx \cdot dy \cdot dz \quad (2)$$

The problem is to determine the probability  $P$  that the assembly of  $N_0$  molecules should be found in the state represented by Equation (2), when the probability that a given molecule has components of length  $x$ ,  $y$  and  $z$  is given by Equation (1). The result found by Wall is:

$$\ln \frac{P}{P_0} = -\frac{N_0}{2} \left( \alpha^2 + \frac{2}{\alpha} - 3 \right) \quad (3)$$

where  $P_0$  is the probability of the most probable distribution. The entropy change due to the extension is therefore:

$$S - S_0 = k \ln P/P_0 = -\frac{1}{2} N_0 k \left( \alpha^2 + \frac{2}{\alpha} - 3 \right) \quad (4)$$

The tension  $F$  is then obtained by applying the thermodynamic relation:

$$F = \left( \frac{\partial W}{\partial l} \right)_T = -T \left( \frac{\partial S}{\partial l} \right)_T$$

giving, for a cylinder of original cross-sectional area 1 cm.<sup>2</sup>:

$$F = NkT \left( \alpha - \frac{1}{\alpha^2} \right) = \rho \frac{RT}{M} \left( \alpha - \frac{1}{\alpha^2} \right) \quad (5)$$

where  $N$  is the number of molecules per cc.,  $M$  the molecular weight, and  $\rho$  the density.

Equation (5) applies for a unidirectional compression as well as for an elongation.

## 2. WALL'S TREATMENT OF SHEAR

A simple shear may be defined<sup>7</sup> by a change of the dimensions of the specimen from  $x$ ,  $y$  and  $z$  to  $\alpha x$ ,  $y/\alpha$  and  $z$ . As before, Wall assumed that the molecular components of length change in the same ratio as the external dimensions. The function representing the distribution of molecular lengths in the state of shear is therefore:

$$p'(x, y, z) dx \cdot dy \cdot dz = \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2[x^2/\alpha^2 + \alpha^2 y^2 + z^2]} dx \cdot dy \cdot dz \quad (6)$$

The result was obtained in terms of the work required to produce a shear deformation  $\sigma \left( = \alpha - \frac{1}{\alpha} \right)$ , namely:

$$W = \frac{1}{2} NkT\sigma^2 = \frac{1}{2} G\sigma^2 \quad (7)$$

from which it is seen that the modulus of rigidity  $G$  appears as a constant. That is to say, the network obeys Hooke's law under shear, though not under elongation.

## 3. KUHN'S TREATMENT OF ELONGATION

Kuhn made the same fundamental assumptions as Wall, but worked from a consideration of the entropy of the single molecule, integrating over the whole assembly of molecules in order to obtain the total entropy. From Equation (1), the entropy  $s$  of a single molecule is given by Kuhn as:

$$s = k \ln p = c_1 - k\beta^2(x^2 + y^2 + z^2) = c_1 - k\beta^2 r_1^2 \quad (8)$$

where  $r_1$  is the distance between its ends. The contribution to the total entropy per cc. due to molecules having length components between  $x$  and  $x + dx$ ,  $y$  and  $y + dy$ ,  $z$  and  $z + dz$  is obtained by multiplying this entropy  $s$  by the appropriate number of molecules, i.e.:

$$s \cdot Np(x \cdot y \cdot z) dx \cdot dy \cdot dz$$

$N$  being the number of molecules per cc. Integration gives the total entropy  $S_1$  corresponding to the unstretched state:

$$S_1 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} N[c_1 - k\beta^2(x^2 + y^2 + z^2)] \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2(x^2 + y^2 + z^2)} dx \cdot dy \cdot dz \quad (9)$$

For the deformed state corresponding to an extension in the  $x$  direction of amount  $\gamma$  ( $= l/l_0 - 1$ ) the entropy  $S'_1$  is represented by the integral:

$$S'_1 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} N[c_1 - k\beta^2(x^2 + y^2 + z^2)] \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2[x^2/(1+\gamma)^2 + (y^2 + z^2)(1+\gamma)]} dx \cdot dy \cdot dz \quad (10)$$

in which the exponential term represents the distribution of molecular lengths after deformation. Integration of Expressions (9) and (10) leads to the approximate relation:

$$S'_1 - S_1 = -\frac{3}{2} Nk\gamma^2 \quad (11)$$

*Entropy due to  $r_2$  and  $r_3$  values.*—The entropy thus determined, referred to by Kuhn as the partial entropy due to the  $r_1$  values, was not considered to represent the whole of the entropy change on extension. He argued that, besides having a "length"  $r_1$ , the molecule may be considered to have a "breadth"  $r_2$  and a "thickness"  $r_3$ , and that it is necessary to take into account also the partial entropies associated with the  $r_2$  and  $r_3$  values. If  $Z$  is the number of links in the chain,  $r_2$  is defined as the distance of the middle link from the line joining the ends, and  $r_3$  as the distance of links numbered  $Z/4$  and  $3Z/4$  (counting from one end of the chain) from the plane containing  $r_1$  and  $r_2$ . Kuhn's method of calculating the entropy due to the  $r_2$  and  $r_3$  values will not be considered here. The result is that an additional entropy of amount  $-Nk\gamma^2$  is introduced for each of these values, so that the total entropy change on extension becomes:

$$S' - S_0 = -\frac{3}{2} Nk\gamma^2 - 2Nk\gamma^2 = -\frac{7}{2} Nk\gamma^2 \quad (12)$$

This leads directly to the stress-strain relation:

$$F = 7NkT\gamma = 7NkT(\alpha - 1) \quad (13)$$

This result does not agree with that of Wall (Equation (5)), the one relation being linear and the other nonlinear. The reasons for this discrepancy will now be considered.

#### 4. CRITICISM OF KUHN'S TREATMENT

*The  $r_2$  and  $r_3$  values.*—The probability function (1) is derived by considering the number of possible configurations of the molecule when one end is fixed at the origin of coördinates and the other is contained within a small volume element  $dx \cdot dy \cdot dz$ . On Kuhn's basis, the entropy is reduced on extension because the number of possible configurations is reduced. In stating the probability in terms of  $r_1$ , he includes all possible configurations and, therefore, all possible values of  $r_2$  and  $r_3$ . The  $r_2$  and  $r_3$  values cannot be considered to have an existence independently of  $r_1$  and to attribute a separate entropy to them is incorrect.

If the  $r_2$  and  $r_3$  values are omitted, Equation (13) becomes:

$$F = 3NkT\gamma \quad (14)$$

Wall's Equation (5) gives for the modulus at zero extension:

$$\left( \frac{dF}{d\gamma} \right)_{\gamma=0} = 3NkT \quad (15)$$

The modified Formula (14) thus agrees with Wall's equation for sufficiently small elongations.

It will now be shown that the remaining difference between the results of Wall and of Kuhn is due to the introduction of an approximation by the latter author.

#### 5. AMENDMENT OF KUHN'S TREATMENT

(a) *Elongation.*—From Kuhn's Equations (9) and (10), the entropy change on extension may be written:

$$\begin{aligned} \frac{\pi^{\frac{1}{2}}}{Nk\beta^5} (S'_1 - S_1) &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (x^2 + y^2 + z^2) e^{-\beta^2(x^2+y^2+z^2)} dx \cdot dy \cdot dz \\ &- \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (x^2 + y^2 + z^2) e^{-\beta^2[x^2/(1+\gamma)^2 + (y^2+z^2)(1+\gamma)]} dx \cdot dy \cdot dz \quad (16) \end{aligned}$$

Insertion of the appropriate values of the definite integrals<sup>8</sup> gives:

$$\frac{\pi^{\frac{1}{2}}}{Nk\beta^5} (S'_1 - S_1) = \frac{3}{2} \frac{\pi^{\frac{1}{2}}}{\beta^5} - \frac{\pi^{\frac{1}{2}}}{2\beta^5} \left[ (1+\gamma)^2 + \frac{2}{1+\gamma} \right]$$

or

$$\frac{1}{Nk} (S'_1 - S_1) = \frac{3}{2} - \left[ \frac{(1+\gamma)^2}{2} + \frac{1}{1+\gamma} \right] = -\frac{1}{2} \left( \alpha^2 + \frac{2}{\alpha} - 3 \right) \quad (17)$$

Equation (17) is identical with Wall's Equation (4), and leads directly to the stress-strain relation (5), without any approximation. The approximation

introduced by Kuhn (valid for small values of  $\gamma$ ) was evidently to write:

$$\frac{1}{1 + \gamma} = 1 - \gamma + \gamma^2$$

and thus to obtain:

$$\frac{1}{Nk} (S'_1 - S_1) \simeq -\frac{3}{2} \gamma^2 \quad (\text{cf. Equation (11)})$$

It is obvious that the formula of Kuhn is valid only for elongations of considerably less than 100 per cent. It is unfortunate that Kuhn did not emphasize the fact that an approximation was involved in the derivation of his apparently linear stress-strain relation.

(b) *Shear*.—Although Kuhn did not deal with the shear deformation, this problem also may be dealt with by his method. Writing the total entropy after shearing in the form:

$$S'_1 = \int \int \int_{-\infty}^{+\infty} N [c_1 - k\beta^2(x^2 + y^2 + z^2)] \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(x^2/\alpha^2 + \alpha^2 y^2 + z^2)} dx \cdot dy \cdot dz \quad (18)$$

and following exactly the same process as in the case of elongation, we obtain:

$$\frac{1}{Nk} (S'_1 - S_1) = -\frac{1}{2} \left( \alpha^2 + \frac{1}{\alpha^2} - 2 \right) \quad (19)$$

which, on substitution of  $\sigma$  for  $\alpha - \frac{1}{\alpha}$  leads to Wall's result (Equation (7)):

$$W = \frac{1}{2} NkT\sigma^2$$

## 6. SOME GENERAL CONSIDERATIONS

The more accurate application of Kuhn's method thus leads to the same stress-strain relations as those derived by Wall. The two methods may be considered to be equivalent mathematically, since they differ only in the particular stage of the argument at which the concept of the entropy is introduced. Wall considered only the entropy to be associated with the whole assembly of molecules; Kuhn, on the other hand, considered that an entropy could be associated with the individual molecule. Wall's treatment must be considered the more satisfactory because it avoids the difficulties encountered in attempting to assign a physical meaning to the entropy of a single molecule.

An equation of similar form to Equation (5) has been derived independently by Guth and James<sup>9</sup>, who state that it represents the experimental data for both elongation and compression of rubber to a close approximation. In using the equations of the kinetic theory, however, it is important to keep in mind the assumptions which form their basis. In Kuhn's statistical treatment of the paraffin molecule, from which all the later developments have proceeded, it is assumed that the distance  $r$  is small compared with the outstretched length of the chain. The formulas derived from the network theory would, therefore, not be expected to apply to a state of deformation in which any important fraction of the molecules were nearly fully extended. They cannot, therefore, be expected to account accurately for the whole of the stress-strain curve of rubber.



It is interesting to note that Equations (5) and (7) contain, implicitly,  $M$ , the "molecular weight" between junction points, but do not specifically contain  $Z$ , the number of links, or  $\theta$ , the supplement of the valence angle (which are included in the parameter  $\beta$  (Equation (1a)). The equations would, therefore, not be affected if the freedom of rotation about bonds were imperfect, since, as Kuhn has shown<sup>3</sup>, a chain of  $Z$  links possessing hindered rotation is equivalent to a chain containing a smaller number  $Z/s$  of freely rotating links (where  $s$  is a small number), provided, of course, there are still enough effective links to justify the application of statistical methods. The same argument shows that the elastic properties of the network will not be affected by the presence of a proportion of nonrotating bonds, such as the C=C bond in rubber.

#### SUMMARY

The treatment of the elasticity of a molecular network by the method of Wall is discussed and is compared with the earlier treatment of Kuhn. It is shown that a more accurate application of Kuhn's method leads to formulas for elongation and shear in agreement with those of Wall.

The author desires to acknowledge his indebtedness to J. K. Roberts for several helpful discussions during the preparation of this paper, which forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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## THE STRUCTURE AND REACTIONS OF RUBBER. A GENERAL DISCUSSION

RUBBER CHEMISTRY AND TECHNOLOGY published, in its July and October 1942 issues, a series of papers comprising a symposium on "The Structure and Reactions of Rubber", held by the Faraday Society, London, May 29, 1942. The papers were followed by critical discussions, which are assembled in the following pages, with references to the corresponding original papers.

### THE INFLUENCE OF CHEMICAL STRUCTURE ON THE IMBIBITION OF LIQUIDS BY RUBBER. I

G. S. WHITBY, A. B. A. EVANS AND D. S. PASTERNAK

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 3, pages 553-559,  
July 1942)

AND

### THE INTERACTION BETWEEN RUBBER AND LIQUIDS. II. THE THERMODYNAMICAL BASIS OF THE SWELLING AND SOLUTION OF RUBBER

G. GEE

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 3, pages 545-552,  
July 1942)

#### DISCUSSION

G. Gee (*Welwyn Garden City*).—The theory of solubility and swelling developed in my paper forms a basis on which I believe we can understand some of the main features of the table of swelling data given by Whitby. Treating the problem as that of the limited miscibility of two liquids, we neglect differences in the entropies of dilution of rubber by various liquids. The extent to which vulcanized rubber swells is then a function of the heat of dilution, becoming a maximum when the heat of dilution is zero (neglecting the limited number of liquids, which may give heat evolution). The heat of mixing of two liquids may be related, at least in simple cases, to the difference between their cohesive energies (Hildebrand, Scotchard) or surface energies (Langmuir). If, therefore, we plot the extent of swelling of vulcanized rubber in a liquid against the cohesion energy of the liquid, we should expect to find a curve showing a maximum at the cohesive energy of rubber. This is very roughly true for Whitby's data, though there are many exceptions, of which the most notable are: (1) the low swelling power of ketones, and (2) the higher swelling power of aromatic compounds relative to aliphatic compounds. Some of the complicating factors were briefly mentioned, and it is proposed to discuss the whole problem at greater length in a paper now in preparation.

D. D. Eley (*Cambridge*).—The amount of swelling of rubber in contact with a liquid is determined by the free energy change associated with the

transfer of 1 gram-mole of solvent molecules from an infinite amount of the liquid to an infinite amount of the rubber:

$$\Delta G = \Delta H - T\Delta S$$

Gee has indicated that, for a range of liquids which swell rubber, differences in  $\Delta S$  may be small. An insight into the  $\Delta H$  term may be obtained by applying a theory of solubility previously published.

(1) Transfer a mole of swelling agent to the gas phase, heat content change  $L$ , where  $L$  is the heat of evaporation of the swelling liquid.

(2) Make a gram-mole of cavities in the rubber substance of the correct size to receive the swelling molecules, heat content change  $H_C$ .

(3) Transfer the swelling liquid from the gas phase to the cavities in the rubber, heat content change  $H_A$ .

$$\Delta H = L + H_C + H_A$$

Whitby's data immediately enable us to draw certain qualitative conclusions. As the size of the molecules increases over a homologous series, the amount of swelling increases and, with the above assumption about the behavior of  $\Delta S$ , this means that, over the series,  $\Delta H$  becomes more negative. Since both  $L$  and  $H_C$  tend to assume larger positive values with increased size of the swelling molecule, and  $H_A$  tends to assume larger negative values, it appears that the  $H_A$  term is of predominant importance in swelling phenomena. It is possible that the swelling of rubber by liquids is analogous to the solubility of gases in water, where the  $H_C$  term is negligible compared with  $H_A$ , and in this case  $\Delta H$  over a series of liquids is determined mainly by  $L + H_A$ .  $L$  is determined by the London forces (roughly measured by the polarizability  $\alpha$ ) and the dipole forces (being larger the larger the dipole moment  $\mu$ ). On the other hand, the interaction of the swelling molecule with neighboring non-polar molecules is but little affected by the dipole moment of the solvent molecule, which in fact tends to retard swelling by increasing the inner cohesion of the swelling liquid measured by  $L$ . This  $H_A$  term depends mainly on the London forces between the swelling molecule and the neighboring polyisoprene chains, and again tends to increase with the polarizability of the swelling molecule  $\alpha$ .

Over a series of liquids which show increasing solubility in rubber, that is, over a series where  $\Delta H$  decreases towards zero or becomes a negative quantity, we may assume that the effect of increase of  $\alpha$  tends to give an increase of  $-H_A$  which outbalances its effect in increasing  $L$ . The two factors,  $\alpha$  and  $\mu$ , may, then, be considered to oppose one another, large  $\alpha$ 's tending to assist, and large  $\mu$ 's to hinder swelling of rubber by a liquid. Since the dielectric constant of a liquid is made up of the sum of two terms involving  $\alpha$  and  $\mu$ , it is clear why we cannot expect the relation suggested by Ostwald to hold.

J. R. Scott (*Croydon*).—In swelling experiments on vulcanized rubber, care is necessary in deducing the true "swelling capacity" of the liquid from the data, in view of the existence of secondary effects that may be of large magnitude. It has been shown that the time/swelling curve consists of an initial (relatively) rapid absorption or saturation of the rubber, followed by a slow increase in swelling, continuing indefinitely at a more or less constant rate ("increment"). The increment is due to a gradual change in the properties of the rubber, which normally arises from oxidation by atmospheric oxygen, and is greatly accelerated by small amounts of oxidizing agents, oxidation catalysts, and certain acids and bases. Examination of some of Whitby's

results by plotting swelling against time, notably for limonene, *n*-heptoic, caprylic and pelargonic acids, benzoyl chloride, *p*-chlorobenzoyl chloride, benzaldehyde, propiophenone, cyclohexanone, citronellol, thiophenol, and  $\beta$ -butyrodichlorhydrin, suggests that the increment was very large and thus responsible for a considerable part of the swelling after 31 or 62 days. To obtain a true estimate of the swelling capacity of the liquid, uninfluenced by changes in the rubber, the "increment" part of the curve should be extrapolated back to zero time.

The statement (paragraph 2) regarding the absence of a clear relation between viscosity and rate of swelling might suggest that these properties are quite unrelated. There is, however, a strong tendency for viscous liquids to be absorbed slowly, and *vice versa*. Thus, among 16 liquids examined there was a highly significant correlation (correlation coefficient + 0.954) between viscosity and "swelling time", expressed as the time required to reach a given fraction of the maximum swelling. This is true of soft vulcanized rubber, but not of ebonite.

G. S. Whitby (*Teddington*).—I was much interested in Gee's treatment of some of the data given in the paper, and hope that he will extend it. With reference to Scott's remarks, it may be pointed out that, while in many liquids the time-swelling curve rises very steeply during the first 24 hours and then only very slowly, in a not inconsiderable number of liquids there is much less contrast in slope between the early and the later parts of the curve, and swelling after 24 hours is much more than a mere "increment". At all events in these latter cases, it is not easy to accept the view that the intercept on the swelling axis made by the later part of the curve should be taken as the "true swelling", and it is difficult to believe that the large increase in swelling after 24 hours is merely a secondary effect due to oxidation.

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### THE PLASTIC-ELASTIC BEHAVIOR OF EBONITE

J. R. SCOTT

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 826-834, October 1942)

#### DISCUSSION

J. R. Scott.—Two points concerning the properties of ebonite should be amplified.

(1) In a set of time/deformation curves at temperatures above 100° C, the "drift" or slope of the upper part of the curve (*cf.* 105° C curve, Figure 2) showed a large and roughly exponential increase with temperature, increasing from 0.04 at 100° C to 0.41 at 125° C (unit = angular degree/min.). This suggests the onset of true plastic (irreversible) deformation at these temperatures, but to decide this point definitely it will be necessary to examine the time/recovery curve to see if there is a permanent residual deformation.

(2) Young's modulus for well-vulcanized ebonite at room temperature is practically independent of its sulfur content between 20 and 35% (the rest

being rubber). This shows that the physical properties of ebonite are not a simple function of its combined sulfur content, as might appear from paragraph 1 (4) of the paper. There is, indeed, much other evidence leading to this same conclusion (see, e.g., Porritt, *Proc. Rubber Tech. Conf., London, 1938*, p. 917).

W. J. S. Naunton.—Scott's views offer an explanation of the useful properties of flexible ebonite made by incorporating polychloroprene with the rubber before vulcanization. The polychloroprene cannot be vulcanized to a rigid product but, on the other hand, the less heat-stable bonds between the ebonite network and the polar polychloroprene network are far stronger than those between the ebonite network and common plasticizers such as mineral oil, with the result that a flexible ebonite with reasonable heat stability is obtained.

R. M. Barrer (*Bingley*).—The formulation of the hypothesis concerning plastic yield of ebonite suggests thermal energy fluctuations as the cause of instability in "secondary bonds". If the "bonds" become unstable when a total energy  $\geq E$  is accumulated in  $f$  degrees of freedom, and if the number of bonds is  $N_0$ , the number in an unstable state should be:

$$N_1 = N_0 \left( \frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} e^{-E/RT}$$

For a given value of  $E/RT$  and  $f$ , one may use this distribution law to calculate the temperature/stability curve of Figure 1 of Scott's paper.

## THERMODYNAMIC STUDY OF THE ELASTIC EXTENSION OF RUBBER

L. R. G. TRELOAR

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 784-789, October 1942)

### DISCUSSION

D. Bulgin (*Birmingham*).—An interesting link with the kinetic theory of rubber elasticity has been obtained from some work now in progress on the structure of carbon black in rubber mixes. The method of investigation includes the measurement of electrical conductivity of rubber containing varying concentrations of different forms of carbon under various temperature, pressure, and elongation conditions. The carbon (gas black) referred to in this communication is of colloidal dimensions (mean particle-diameter from electron microscope measurements 300 Å.), and as a first approximation the system may be regarded as a colloidal dispersion of carbon in rubber.

The relationships between electrical conductivity and carbon concentration, and electrical conductivity and temperature at zero pressure and elongation are:

$$(C)_T = Q^2/K \quad (C)_Q = T^2/K_1$$

where  $(C)_T$  and  $(C)_Q$  = conductivities at constant temperature and concentration,  $Q$  = concentration,  $T$  = temperature ( $^{\circ}\text{K}$ ) and  $K, K_1$  = constants.

From these relationships:  $Q/T$  = constant, which is comparable to the gas equation:  $pV/T$  = constant at constant volume.



The change of  $Q$  per  $^{\circ}\text{K}$  is 0.0035, which is very close to the gas coefficient (0.00366). It may be concluded that the carbon particles constitute a colloidal system in Brownian movement in the rubber due to the kinetic movements of the rubber molecules.

Conductivity does not appear to arise directly from the motion of the carbon particles, since the system obeys Ohm's law for normal voltages, and is also subject to thermal hysteresis effects if the system is not mechanically disturbed on passing from a higher to a lower temperature. These facts suggest that forces exist between the carbon particles, and give rise to a quasi-solid structure of carbon which enables electronic conductance to take place.

## THE KINETICS OF RUBBERLIKE ELASTICITY

D. D. ELEY

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 3, pages 438-445, October 1942)

### DISCUSSION

D. D. Eley (*Cambridge*).—In introducing my paper, I should like to note the two ways in which we may expect the treatment to be further developed. In viscous flow and in elastic orientation, we have considered mechanical movement to be characterized by a relaxation time  $\tau$ , viz:

$$\tau = A e^{\Delta H^*/RT}$$

First, it is possible that  $\tau$  may be a function of stress, *i.e.*,  $\Delta H^*$  a function of stress, as first suggested by Maxwell, and recently developed by De Bruyne for plastic flow.<sup>1</sup>

Secondly, a whole band of relaxation times may occur, *i.e.*, instead of relaxation occurring through the movement of a segment of definite size, a whole range of segment sizes must be considered. Kirkwood and Fuoss<sup>2</sup> have recently shown that a whole band of relaxation times is required to explain the dielectric dispersion data in polyvinyl chloride-plasticizer systems. Simha has shown how to obtain the distribution function of the relaxation times, in the mechanical case, from the stress-strain diagram.

However, in cases where a broad difference of behavior exists, such as that between viscous and elastic phenomena in rubber, it appears legitimate to base a simple molecular analysis on the concept of single relaxation times.

C. W. Bunn (*Norwich*).—With regard to the effect of crystallization on elastic properties, I should like to point out that when fibres or strips of crystalline polymers, such as rubber hydrochloride or polyethylene, are cold-drawn (the length becoming some four or five times the original length) and then are subsequently warmed to temperatures just below their melting points, they retract to their original dimensions, or very nearly.<sup>4</sup> The x-ray photographs of such materials show that they contain a good deal of crystalline material—how much, we do not know, but certainly a fair proportion of the whole; in other words, a fair proportion of the material consists of regions in which sections of molecules are perfectly straight (probably for some hundreds of Å.U.), and packed parallel to each other in a precise manner. This retraction of partly crystalline substances (which, though less than in the case of fully stretched rubber, is of the same order of magnitude) should be remembered



in any attempt to correlate the elastic properties of high polymers with their structure. It does at any rate show that for high elasticity it is not necessary that molecules be curled in random configuration over the whole of their length, but that quite long sections of them may be straight. In the theoretical treatment of elastic properties, possibly these properties may be attributed entirely to the amorphous regions (in which sections of molecules may be curled at random), the crystalline regions being regarded merely as diluting the amorphous material.

J. R. S. Waring (*Manchester*).—This and the following paper by Tuckett are of particular interest to us, as they refer to the alteration of mechanical properties with increased rate of alternation of stress. We have been studying the effect of frequencies above 100 c.p.s. on a range of rubbers, including synthetic materials, and we have found that those rubbers which show a pronounced temperature dependence of properties, also show marked mechanical "dispersion". It would be of interest to know if there is any exact equivalence, on theoretical grounds, between temperature and frequency. For many practical purposes—tires, engine mountings, etc., rubber is distorted under rapidly alternating stresses, so that these questions are of immediate interest. There seems to be some relation between these properties and the polar nature of some of these rubbers, which brings one to the great importance of really planned work of correlation between "electrical" and "mechanical" dispersion over a wide field. This, we would suggest, would be as valuable as the suggestions for future work made in these papers.

It would be of interest to know in this connection whether the rubber referred to by Eley as showing no electrical dispersion was cured or uncured. Zwicker<sup>5</sup> has described some experimental work which shows electrical dispersion with some natural rubber compounds.

L. R. G. Treloar (*Welwyn Garden City*).—Eley bases his work on the experimental data of Alexandrov and Lazurkin. It should be pointed out that the latter authors expressly point out that their  $\log \tau$  vs.  $1/T$  relationships are linear over only a small temperature interval, and that energies of activation cannot, therefore, be derived from them. In view of this warning, does Eley consider the procedure he has adopted to be justified?

A fundamental difficulty appears to arise in the interpretation of the molecular "segment". Assuming the segment size to be the same both for viscous flow and for the elastic orientation process, Eley concludes (from the different energies associated with the processes) that 31 k.cal. must arise from rotations about C—C bonds amounting to 10 per segment. But if the segment has 10 internal axes of rotation it cannot be acting as a kinetic unit in the sense in which the term "segment" is understood, i.e., the conclusion would appear to have destroyed the premise on which it was based.

Finally, a word about the reference to crystallization. The statement in the last paragraph is inaccurate. Crystals are not dispersed as neutral masses along the molecular chains, but strongly affect the intermolecular forces, and may exert a profound effect on the mechanical behavior of rubber.<sup>6</sup>

G. S. Whitby (*Teddington*).—The author's discussion appears to be based, fundamentally, on the idea that in rubberlike materials in an unstrained condition the molecules are coiled—have a helical form. Is it not difficult to picture such coiled molecular chains in the case of materials such as polystyrene (which shows rubberlike elasticity when warmed or when mixed with a plasticizer) where every second carbon atom of the chain carries a large substituent, viz., a benzene ring? In making this remark, I am not unaware of de Boer's prior discussion of the possible sterical configurations of the polystyrene molecule<sup>7</sup>.

R. C. Seymour (*Manchester*).—Smallwood and Eyring's interpretation of Mooney's data suggests that viscous flow of unvulcanized rubber proceeds via the surmounting of an energy barrier of height:  $\Delta H_{\text{visc.}} = 10.2$  k.cal. Alexandrov and Lazurkin's figure gives a barrier height of  $\Delta H^*_{\text{el}} = 38$  k.cal. per mole for the rate step in elastic relaxation.

In unvulcanized rubber, plastic flow is more probable because of the smaller energy barrier which has to be overcome. Suppression of plastic flow as we pass along the plastic-elastic scale in the direction of increasing elasticity is, then, explained by an increase in  $\Delta H_{\text{visc.}}$ , so viscous flow is increasingly less probable. Cross-linking has the effect of decreasing plastic flow due, as Eley correctly indicates, to enhanced values of  $\Delta H_{\text{visc.}}$ . If  $\Delta H_{\text{visc.}}$  is indeed related to the latent heat of vaporization required to produce a hole in the high polymer, sufficient to allow the movement of a segment, does not a larger value of  $\Delta H_{\text{visc.}}$  require movement of a larger segment? One cross-linkage involves two neighboring segments.

Eley does not seem to have given sufficient attention to the fact that, whether we deal with vulcanized or unvulcanized rubbers, we still have unknown combinations of plastic and elastic components, the chief differences in these two states being due to the different probabilities for viscous flow in the two cases.

Since this is so, for a given value of  $\Delta H^*_{\text{el}}$ , the contribution made by  $\Delta H_{\text{el}}$  (1) is greater, the higher the degree of cross-linking. Therefore the contribution of  $\Delta H_{\text{el}}$  (2) (supposedly due to rotations of C—C bonds) must be correspondingly less.

Of further interest, has Eley considered the possibility that while viscous flow is a continuous process, elastic relaxation may indeed be a noncontinuous process, consisting of a series of jumps over energy barriers of varying heights corresponding to different relaxation times? If this were the case, treatment of the rate step in elastic relaxation requires a form of Eyring's conception modified in some way similar to the technique of passing from Maxwellian statistics to the quantized statistics of Fermi and Dirac in wave mechanical theory.

D. D. Eley (*Cambridge*).—In reply to Waring, the stress-frequency at which rubber loses its characteristic elasticity may be obtained from the paper by Alexandrov and Lazurkin cited in my paper, or calculated from the entropies and energies of activation for the elastic process given by me, which are of course derived from their data.

In reply to Treloar, I had of course noted that the activation energy term was not independent of temperature. This behavior is shown not only in viscous flow and elastic orientation processes in high polymers, but also in many chemical reactions. It seems to me, however, legitimate to compare the viscous flow and orientation activation energies, even if they are not strictly independent of temperature, as long as they are derived from experiments made over the same, or nearly the same, temperature intervals.

In Eyring's theory, the idea of a segment in viscous flow is based, not primarily on a mechanical model, but on the necessity of accounting for the observed activation energy, which with increase in length of a hydrocarbon or analogous (relatively nonpolar) chain, reaches a maximum of about 10 k.cal. per mole. For small molecules experiment establishes a definite dependence of  $\Delta H_{\text{visc.}}$  on molecular size (or more accurately, intermolecular cohesive forces, which of course tend to run parallel to molecular size). This is expressed by  $\Delta H^*_{\text{visc.}} = 1/3 L$  for spherical molecules,  $\Delta H^*_{\text{visc.}} = 1/4 L$  for nonspherical

molecules, where  $L$  is the latent heat of evaporation. In the simplest instances negligible, or zero, intramolecular rotational activation occurs, and  $L$  may be attributed entirely to intermolecular bonds. On Eyring's theory,  $L$  (more strictly  $L - RT$ ) may be equated to the energy required to form a hole of molecular size in the liquid, and the corollary is that, in viscous flow, it is necessary to make a cavity in the liquid a definite fraction of the molecular size before flow of the molecule can occur. The relation  $\Delta H^*_{\text{visc.}} = 1/4 L$  would appear to hold from 1 to 5 C atoms, and we may conclude that negligible rotational activation occurs for the 5 C atom compound<sup>8</sup>. That is, a similar small degree of intramolecular rotation occurs both in the liquid and in the gas phase. The determination of segment size in viscous flow of polymers is based on this conclusion. The energy of activation is compared with the latent heat of evaporation of the monomer, *i.e.*, the segment is the kinetic unit based on the assumption that in viscous flow the same degree of rotational excitation occurs as in the evaporation of the monomer. The previous argument shows that negligible rotational excitation occurs in the latter case. So, in my theory the extra 31 k.cal. for elastic over viscous processes is to be attributed strictly to the excess rotational excitation in elastic over viscous processes.

Summarizing, it appears therefore that Eyring's theory, on semi-empirical grounds, enables us to separate in a simple fashion the influence of cohesive forces and intramolecular rotational excitation in relaxation processes. The cohesive forces are to be regarded as determining the segment size in this theory. A further rotational activation of the segment may occur without invalidating the theory, as long as all the cohesive and rotational activation occurs at the same instant. In this way the segment behaves as a distinct kinetic unit, and may not be split into smaller segments or kinetic units. Fundamentally, a segment or kinetic unit is just that part of a chain which has to receive a certain activation energy at one instant for the elementary flow process to occur. A complete chain of  $n$  segments can receive  $n$  separate and successive energy instalments of value  $\Delta H^*_{\text{visc.}}$  for the whole chain to show a displacement.

I accept the criticism about crystallization. Although I have had no time to test my suggested relationship, the considerations of Alfrey,<sup>9</sup> of which I was unaware at the time of writing, would suggest that it is not valid.

In reply to Whitby, I can see no reason in principle why polystyrene chains should not coil up sufficiently to give a kinetic elasticity. This point is further discussed by Tuckett.

In reply to Bunn, the polyethylene observations appear at first sight difficult to reconcile with the kinetic theory of elasticity. This theory, would, however, appear to be the only one capable of accounting for the experimental facts with regard to rubber, as pointed out in the paper by Treloar. It is, of course, also possible to obtain highly elastic phenomena through energetic mechanisms, *e.g.*, the network mechanism of Van Dongen.<sup>10</sup> It would be interesting in this connection to obtain the temperature dependence of Young's modulus for polyethylene. It would also be interesting to know the fraction of crystalline polymer in polyethylene below the "fusion" temperature. This is not necessarily unity, and the extension of polyethylene below 115° C may contain a contribution from the kinetic elasticity of the amorphous material, if this is present. "Crystalline" rubber, for example, appears to contain a considerable percentage of amorphous material<sup>11</sup> and shows considerable extensibility.

In reply to another question, it is possible, with Eyring's theory, to picture

viscous flow diagrammatically for simple spherical molecules. Here the molecule can easily be visualized as moving from one lattice point to a neighboring point in the liquid, treated as quasi-crystalline. It is not so easy to picture the flow of long chains, moving as a result of the coöperative displacement of segmental units. The argument for segments is based on energy considerations, rather than on a mechanical model (for details, see my reply to Treloar). The difficulty of visualizing the detailed motion by a sketch on the blackboard does not seem to be an argument against the theory. Actually the motion of these molecules must be very complicated. In viscous flow of polymers without cross-bonds, at low rates of shear, it does not appear necessary that the molecule should have to straighten to flow. Molecules will be continually entangling and disentangling, a net displacement in direction of flow resulting. At high rates of shear, a certain amount of orientation might be expected. In vulcanized rubber, where viscous flow follows on vigorous extension, the determining factor will be the cross-bonds, holding the elastically orientated molecules in position. As these cross-bonds break the parallel chains will be able to slide over each other.

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### THE KINETICS OF HIGH ELASTICITY IN SYNTHETIC POLYMERS

R. F. TUCKETT

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 3, pages 430-437,  
July 1942)

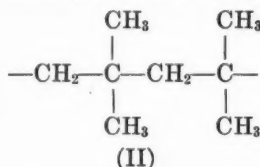
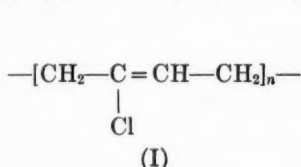
#### DISCUSSION

P. J. Garner (*Birmingham*).—Alexandrov and Lazurkin's treatment of high elasticity expounded by Eley and by Tuckett applies only to supercooled liquids. It must be emphasized that the equilibrium state of rubber at low temperatures is crystalline, the melting point being between + 40° and 50° C. A high elasticity temperature of - 70° C for rubber is obtained only when it is supercooled, which is made possible by the avoidance of large deformations (> 15%) which would induce crystallization. The useful properties of rubber under normal conditions are largely due to crystallization on stretching. The effect of vulcanization in lowering the temperature range of usefulness is probably connected with the suppression of crystallization. This fact is the basis of the T-50 test for vulcanization.

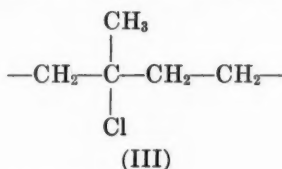
Tuckett's theory relating elastic behavior to molecular structure illustrates the dangers of oversimplification of the problem. The existence of gutta-percha is inconvenient to most theories, and it is generally ignored. Any satisfactory theory must account not only for the properties of rubber, but

also of both  $\alpha$ - and  $\beta$ -gutta-percha, all of which are polyisoprenes. Furthermore, it is incorrect to assign a rubberlike nature to chlorinated rubber as, of course, it is very brittle at room temperature and has a high elasticity temperature of about 100° C.

Then, again, the high elasticity of polychloroprene (I) is assigned to the



polar chlorine atoms being too far apart to affect each other and so to restrict rotation, and in polyisobutene (II) it is assumed that the nonpolar character of the side groups permits rotation in spite of their proximity. Yet rubber hydrochloride (III), in which a nonpolar methyl group is added to the poly-



chloroprene structure in which the Cl atoms are supposed to be too far apart to interfere, is crystalline at room temperature and has a high elasticity temperature of + 95° C.

Another example of the danger of these simple ideas of free rotation is provided by the homologous polymethacrylates; polyethyl methacrylate having a lower high elasticity temperature than methyl whereas one would expect the rotation to be further restricted.

R. M. Barrer (*Bingley*).—The discussion of this and the previous paper has shown a vagueness concerning the way in which a coiled long chain may diffuse. Consider, in the two-dimensional analog, a single chain (Figure 1). In configuration A, the centre of gravity of the chain is shown. The chain reorients itself to give configuration B, and the centre of gravity is seen to have moved forward a distance  $x$ . In the two-dimensional case, such a reorientation would require bond-deformation, but in the three-dimensional case the reorientation may easily occur by partial or free rotation round C—C bonds, without deformation of bond angles.

It is also advisable at this point to summarize the main features which contribute to rubberlike elasticity. From the molecular viewpoint elasticity requires or is favored by:

- (1) Relative apolar chains;
- (2) Very long chains;
- (3) Relatively apolar side chains ( $\text{—Cl}$ ,  $\text{CH}_3\text{—}$ ,  $\text{C}_2\text{H}_5\text{—}$ ,  $\text{C}_6\text{H}_5\text{—}$ );
- (4) Special kinks in chains introduced, for example, by double bonds;
- (5) No cross-linking, or not too extensive cross-linking, by chemical bonds.

Referring to (1) and (2), the chains must be sufficiently long to become thoroughly entangled, and must not interact strongly enough to crystallize. The rubber is then a fluid in one sense, but the great chain length immobilizes



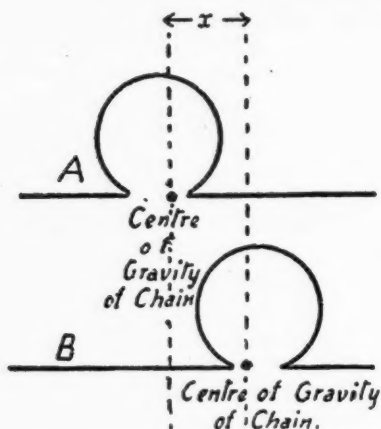


Fig. 1.

the chain as a whole, though intermeshing. In shorter chains, onset of rotation is not enough to produce elasticity. Above certain temperatures long chain hydrocarbons rotate in their crystals, but develop no rubberlike or even fluid properties.

At least two effects may be ascribed to (3):

(1) There is the steric hindrance to rotation discussed by Tuckett, which decreases fluidity.

(2) The side chains help to prevent easy crystallization by making close packing more difficult. They therefore increase fluidity which, coupled with the intermeshing of coiled very long chains, renders the polymer elastic. The double bonds, by introducing unavoidable special kinks in the chains, also reduce the ease with which they may pack together and crystallize and so favor elasticity. For example, of the polymers:



the first is inelastic and waxlike at ordinary temperatures; the two latter are elastic. Similarly, Nylon polymers without side chains are inelastic, but when suitable side chains are introduced a rubberlike polymer may be obtained.

Referring to (5), it is clear that cross-linking serves to reduce plastic deformation, but if not present to a too great extent may not impair rubberlike elasticity. Excess cross-linking, as in ebonite or poly-*p*-divinyl benzene, destroys elasticity.

C. W. Bunn (*Norwich*).—In considering the "freezing points"  $T_F$  of different high polymers and their relation to the flexibilities of the molecules, it does not appear to be sufficient to take into account only the interaction of the side chains on each other. This is shown by the fact that polyethylene, which has no side chains, has a high freezing point (115° C) whereas polyiso-



butene, which has a pair of methyl groups on every other chain carbon atom, has a very low freezing point ( $-65^{\circ}\text{C}$ ). Evidently, there must be some other factor, and I suggest that this other factor is the potential barrier associated with the preferred (staggered) position of the bonds themselves<sup>1</sup>. At any rate, by assuming that both these factors play a part, it is possible to explain some otherwise puzzling phenomena, such as the low freezing point of polyisobutene—for the two factors may sometimes act in opposition and so cancel each other. If a model of the polyisobutene molecule is made, it will be found that, if the configuration is such that the bonds of linked carbon atoms are staggered, the methyl side groups are overcrowded, while if (by rotation round the chain bonds) the methyl side groups are given greater clearance, then the bonds of linked carbon atoms are no longer staggered; thus the bonds prefer one configuration, while the methyl side groups prefer another, the net result being that all configurations have much the same energy, the barriers to rotation are small, and the freezing point low.

G. Gee (*Welwyn Garden City*).—I am not clear whether Table V is intended to show the effect of chemical cross-linking, but I should prefer to regard the observed rise of the high elasticity limit of rubber as due to the combination of sulfur. I do not see how a relatively small number of cross-links could influence the rotation of the main part of the rubber chain. It would be interesting to compare the high elasticity limits of two rubbers of different combined sulfur content, vulcanized to the same state of cure.

G. D. Coumoulos (*Cambridge*).—In a paper to be published shortly, full account of electron-diffraction examination of polyacrylate and -methacrylate esters and polyvinyl acetate is given. The patterns of multilayers and thin lenses of these polymers reveal the fact that it is the side chains that give the major contribution to the diffraction features; the polymers are in the liquid state, and no crystalline features appear even on stretching. The side chains tend to orientate their axes parallel to one another and take up the position of close-packing. A molecular configuration is suggested, in which the chief long chain is a plane zig-zag form and the side chains hang alternately on either side of this plane in the 1, 3, positions (Figure 2). This configuration for

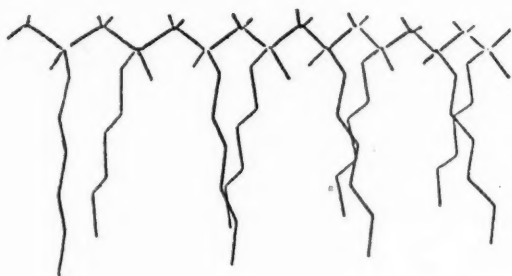


FIG. 2.

polymers with long side chains presents the following differences with respect to rubber:

(1) No crystalline features; (2) no double bonds; (3) no cross-linkings. This configuration further explains the different elastic properties of the polymers from the nature of their side chain: Methacrylate, methylmetha-

crylate, and polyvinyl acetate with side chains of the same length have different properties; our suggested configuration attributes these differences to the different packing of the polar groups in the side chains. It is shown also that by increasing the length of the side chains, these become more flexible. However, over a certain length they lose their flexibility and pack more regularly, because the distortion apparent in the 3 to 4 carbon atom side chains does not influence the longer chains.

A. Charlesby (*Imperial College, London*).—In attempting to relate the elastic properties of a linear polymer to the structure of each individual molecule considered separately, one inevitably meets the following difficulty. If the freedom of rotation about the single C—C bond is simply restricted by the interaction of the side chains, the effect of increasing the length of these chains in any series of polymers should be to produce in a stiffer polymer. This is, however, not the case. In methacrylate polymers, for example, the stiffness and elastic limit decreases rapidly with the length of the chain from methyl to butyl. This presumably corresponds to a decrease in  $T_E$ .

An alternative model provides an explanation of this decrease. If the main part of the resistance to strain arises from intermolecular forces, these will in general be weaker in polymers with long side chains, since the main bulk of two adjacent chains then lies further apart. It is possible to consider the internal structure of a polymer as comprising mainly a large number of pseudocrystalline regions formed by the packing together of small portions of polymer chains which lie in a suitable orientation. These regions can only be extensive with polymers such as polydichlorethylene, which have a symmetrical structure, and which are consequently crystalline. In other, "amorphous", polymers these crystalline regions may be estimated to comprise only about a hundred monomeric units or less. At low temperatures, the cohesion of these crystalline regions prevents high elastic deformation, but at higher temperatures the smaller groupings melt, and considerable deformation is then possible.

The remaining few but larger crystalline regions do not, however, melt, and, bound together by portions of the polymer chains, serve to restore the initial shape when the external stresses are removed. Plasticity and viscosity can be related to the tendency to recrystallize in a new but less stable orientation. This outlook relates the high elasticity temperature directly to the melting point of crystallites rather than simply to the steric interference of side chains, and hence serves also to explain the elastic properties of polymers, such as polyethylene and polydichlorethylene.

Physical evidence can be adduced for this hypothesis. Thin films of orientated polyethylene are crystalline at ordinary temperatures, but show an apparently amorphous structure (by electron diffraction) at temperatures in the neighborhood of their melting point. If a film is raised to a temperature of up to 40° C above its melting point, and recooled, its initial orientation reappears. This can only be due to the survival, in the liquid state, of some memory of its initial structure. This survival can best be explained by the retention within the liquid of some part of the crystal structure, if only on a statistical basis.

D. J. Crisp (*Cambridge*).—It has been suggested that, in rubbers and rubber-like substances, the flexibility of the main chain is considerably influenced by the nature and position of side groups. I would like to mention some work on surface films of certain polymeric substances which support this view.

Polymers of the acrylate and polyvinyl series are found to spread uniformly on aqueous substrates giving monomolecular films at low pressures. The

properties of these films depend on (1) the interaction of the polar group with water, causing spreading and expansion. Substances with only weak polar groups, such as polystyrene, rubber, chloroprene, do not spread.

(2) The flexibility of the chains, which is evidenced by finite pressures, due to kinetic agitation, at relatively large areas of the order of 100–150 (Å.U.)<sup>2</sup> per residue.

(3) The interaction of chains with each other, due to nonpolar forces, leading to condensation of the films. This can be reduced at an oil-water interface.

Thus polyvinyl acetate and acrylates give fluid expanded films, whose force-area relation follows a curve asymptotic to the area axis; while the presence of a methyl group opposite the side chain, as in methacrylates, reduces the flexibility and increases the cohesion. This makes spreading less perfect, and the resulting films are coherent and show a sharp rise in pressure at a fairly definite limiting area.

It is interesting to recall that Adam, using films of cellulose ethers and esters, obtained a similar result; the presence of benzene rings in the side groupings precluded freedom of movement from the cellulose units.

Experiments show also that the length of the alkyl radical in the side chain of a polyester reduces cohesion to a minimum at 3 or 4 carbon atoms. Thus propyl acrylate gives a more expanded film than either ethyl or butyl acrylates, and in the methacrylate series expansion occurs progressively to the butyl member, while octadecyl methacrylate gives films more closely resembling ethyl and methyl methacrylates. Presumably the alkyl radical first reduces cohesion by separating the main chains from each other, but long aliphatic chains will introduce strong attractive forces which counteract the initial effect.

Both in physical properties and in their effects on phase boundary potential, the films closely parallel those of long chain ester compounds.

R. F. Tuckett (*Cambridge*).—The multiplicity of points raised in the previous discussion makes it impossible for me to reply individually to each one, and I shall content myself with a general discussion. The paper, as originally presented, put forward two main suggestions. The fundamental hypothesis was that there existed a close connection between the onset of high elasticity in a polymer and the extent of free rotation in the chain molecule, the latter being determined by steric and interchain effects; this was deduced from a variety of other physical data, and the discussion has not diminished my faith in its essential validity<sup>2</sup>. The second point, namely, the connection between molecular structure and free rotation, was admittedly a bit more speculative, and here it may be that the picture is not so simple as was first suggested. I would be the first to admit that simple concepts based on steric considerations are not in themselves sufficient to explain the various high elasticity temperatures encountered, but they do correlate a number of diverse facts, *e.g.*, the acrylate-methacrylate differences and the low  $T_E$  value of a 2:1 styrene butadiene copolymer.

On the other hand, some molecules do not fit very well into the scheme. Polyethylene is difficult to explain on any general theory, though the ease with which it crystallizes makes the assessment of its elastic properties difficult—polyisobutene also seems to be an awkward case to some people. Rubber hydrochloride, about which my information was not as accurate as it might have been, definitely does not come into line with the theory, though it is difficult to see how it differs essentially from chloroprene in this respect.

The case of the various acrylates and methacrylates shows that a simple steric theory may not be adequate, and that here the determining factor is the interaction between different chains. From the discussion, several points arise; the first is that softening temperatures which fall progressively as the methacrylate series is ascended must not be confused with high elasticity ( $T_E$ ) values—it will be shown elsewhere that softening points essentially represent iso-viscous states and hence depend on molecular size;  $T_E$  values above a minimum chain length are independent of it; for the range of molecular weight over which this is true, Ueberreiter gives 33,000 to 484,000 for polystyrenes.

The effect of changing the side chain length in the acrylates and methacrylates is certainly not a simple steric one, and in this connection the complementary lines of investigation initiated by Coumoulos and Crisp seem to be extremely promising. Crisp's work indicates clearly the importance of the interaction between different chains in determining elastic properties, a point which was emphasized in my original paper in the plasticizer section—a large side chain such as butyl may, in this respect, almost function as an internal plasticizer. It would be extremely interesting to study the effect of temperature on the shape of Crisp's unimolecular films a transition from the coherent methacrylate to the expanded acrylate type as the temperature is raised would be good evidence for the original hypothesis.

In reply to a question by Whitby, Ueberreiter's  $T_F$  values show a spread of  $\pm 5^\circ \text{C}$ , but a discrepancy of  $15^\circ \text{C}$  would seem to require another explanation. Two suggestions can be made; one is that a small amount of residual monomer will depress  $T_F$  considerably (Ueberreiter's specimens were carefully purified from low molecular products by reprecipitation)—the second is that it might be due to the almost complete suppression of branching—this effect has not been considered in the treatment but would be expected to have the same general result as cross-linking though on a much smaller scale.

In reply to Gee, I think that the sulfur in vulcanized rubber, if not acting as a cross-linking agent, but rather as a strongly polar addendum to the isoprene unit, would increase  $T_F$  by cutting down free rotation; my own knowledge of modern theories of vulcanization does not, however, permit a differentiation between the two possibilities.

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- <sup>1</sup> Kistiakowsky, Lacher and Ransom, *J. Chem. Physics* **6**, 900 (1938); Bunn, *Proc. Roy. Soc. A* **180**, 67 (1942).  
<sup>2</sup> Incidentally, Mark has recently come forward with a very similar suggestion (cf. *Ind. Eng. Chem.* **34**, 449 (1942)).

#### PERMEABILITY IN RELATION TO VISCOSITY AND STRUCTURE OF RUBBER

RICHARD M. BARRER

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 3, pages 537-544,  
July 1942)

#### DISCUSSION

R. F. Tuckett (*Cambridge*).—The abnormally high entropies of activation ( $\Delta S^*$ ) discussed by Barrer for diffusion in polymers compared with that in simple liquids are based on a value for the mean free path ( $\lambda$ )  $\sim 10^{-8}$  cm.

(1 Å.U.). In view of recent discussions on viscous flow of macromolecules in terms of segmental motion, it would seem more appropriate to substitute a much larger value for  $\lambda \sim 10 + 100$  Å.U. This possibility has already been envisaged by Barrer but rejected by him in favor of an explanation involving activation through a number of degrees of freedom on analogy with the classical theory of "fast" unimolecular reactions. As this theory now tends to be discarded in favor of some explanation based on the transition state hypothesis, it would seem that any treatment of a discrepancy based on the degrees of freedom concept is to be regarded with suspicion nowadays. Eyring (cf. "The Theory of Rate Processes", p. 544) has also discussed the high value of  $\Delta S^*$ , and has concluded that breaking of bonds occurs in the diffusion process, though he admits the difficulty of visualizing this in the case of helium diffusion.

The above puzzling features arise out of the assumption of a low value for  $\lambda$ , but if a higher value of the order of that suggested for segmental length is assumed,  $\Delta S^*$  retains a normal value. The hypothesis that  $\lambda$  is much greater than the diameter of the diffusing molecule may also offer an explanation of why the energy of activation for diffusion in polymers is almost independent of the size of the diffusing molecule over a wide variation of the latter (cf. Barrer's  $E$  values for various gases through unvulcanized rubber).

Although in liquids there is a close connection between diffusion and viscosity, this is only because the unit of flow is the molecule. A similar simple relationship would not be expected for diffusion through polymers for the following reasons. If one assumes some sort of segmental motion in viscous flow, intersegmental coöperation must occur if the chain molecule as a whole is to move in the direction of applied stress; thus, the viscosity of a polymer is some function of its molecular weight: diffusion, however, occurs through the movement of single segments only—the remainder of the chain does not enter into the process. Hence, one would not expect a connection between diffusion constant and macroscopic viscosity, but rather one with that portion of the viscosity constant which depends on molecular structure only, and not on chain size.

Even so, the problem may not be as simple as at first thought. The connection between diffusion and viscosity in polymers is based largely on the identity of the respective energies of activation for the two processes; this is so for rubber, so far the only case where a comparison has been made. For polyvinyl acetate, such an identity does not exist—for hydrogen diffusion,  $E$  has the usual value  $\sim 10$  k.cal., but for viscous flow it is  $\sim 20$ –25 k.cal., this value being free from elastic effects. This might be taken as indicating a smaller segment size for the diffusion process, but even so, I believe that  $\lambda$  will be much greater than  $\sim 1$  Å. as suggested by Barrer.

R. M. Barrer (*Bingley*).—In my first interpretation of the diffusion data, a large mean free path of the solute atom was given as an alternative to the zone of activation. The data, however, require mean free paths as large as 100 Å.U., and since one can give no physical interpretation to mean free paths of this order in a substance as dense as rubber, I have abandoned this interpretation in favor of the zone theory. My data gave values of the Arrhenius energy of activation,  $E_A$ , largely independent of the identity of the simple solute molecule (He, A, N<sub>2</sub>, H<sub>2</sub>). This I regard as evidence in favor of the zone theory, since most of the energy is absorbed in loosening the surrounding medium, and so is largely independent of the nature of the diffusing small atom or molecule. Tuckett's observation that, for a particular polymer,  $E_A$  for diffusion of simple solutes and for viscous flow are not the same is of interest.



More numerous, accurate and reproducible data of this kind are required, measured in the elastic range of the polymer, before one can draw satisfactory conclusions. In the inelastic range, diffusion down intermicellar boundaries may become important. Exact correspondence in  $E_A$  and optimum zone size would not be observed, however, save for self-diffusion and viscous flow, although in rubber it has been found that the differences are also small for diffusion of simple solutes and viscous flow.

## RUBBER PHOTOGELS

W. J. S. NAUNTON

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 835-842, October 1942)

### DISCUSSION

G. S. Whitby (*Teddington*).—In 1925 I undertook the fractionation of raw rubber by allowing resin-freed smoked sheet to diffuse, fractionally, into benzene. The fractions differed in viscosity (at the same rubber content), and I thus satisfied myself as to the considerable degree of heterogeneity which exists in natural rubber. I refrained, however, from publishing the data, because of the disturbing observation (which I felt required further study, but which, it proved, it was not possible for me to undertake) that solutions of some of the fractions which had been kept in brown stoppered bottles in a cupboard for one summer had gelled when examined in the autumn. Air was present in the bottles. I wonder whether Naunton can explain such an observation: the nonphotogenic gelling of rubber solutions?

H. P. Stevens (*Beccles*).—Since publication of my original paper on Photogels<sup>1</sup>, I have redetermined the rate of gelling of milled and unmilled rubbers, and find that, by rigorous exclusion of air, the rate is reduced by milling, always provided one deals with the same rubber sample. The figures given in my paper (Table V, p. 223) were obtained with sols insolated in contact with a little air. On the other hand, rates of gelling are specific to the particular rubber, and vary considerably with the specimen. I have come across milled rubbers which gel faster, under like conditions, than unmilled. Naunton also gives some results which do not confirm his opening statement in the latter part of section (e), *e.g.*, the gel fraction which took seven times as long to gel after being brought into solution, as the masticated rubber from which it was made, and the sol fraction which took the same time as the original.

Naunton's experiments with hydroquinone and sulfur which at first sight do not appear to confirm mine, were carried out under different conditions; in particular Naunton used a sensitizer, namely, 20 per cent of benzophenone on the rubber. It would be difficult to foresee what reaction would take place between hydroquinone and benzophenone when a mixed solution is irradiated. The use of a sensitizer therefore introduces complications and may well lead to different results from those which I obtained in a single solvent. The great bulk of Naunton's observations, where they cover the same ground, are in consonance with mine. I do not agree with Naunton that the solvents and sensitizers which he used yield a vulcanized rubber. The properties of such dried photogels are quite unlike even very slightly vulcanized rubber. They are more like cyclized rubber and some rubber reaction products. It is possible



to obtain a type of vulcanized rubber by photochemical action with certain catalysts; but these do not act as sensitizers in photogelation, or do so to only a limited extent. I reserve further discussion until I have completed the experimental work on this subject which I have in hand.

With reference to Whitby's observation, the rubber was presumably freed from resin by acetone extraction previous to fractionation. During this operation the rubber would be exposed to light. I have found that insolation of rubber by itself renders it insoluble in benzene. In fact, the separation of a photogel is due probably to the formation of an insoluble rubber product or modification which, therefore, separates. This observation is dealt with in a paper which I have already submitted for publication. Hence the gelling of some of Whitby's fractions in the dark may have been caused by previous insolation of the rubber during acetone extraction.

Further, since acetone extraction removes antioxygens, peroxides may be present in the acetone-extracted rubber. Benzoyl peroxide causes gelling in the dark. Other peroxides may be expected to have a similar action.

W. J. S. Naunton (*Manchester*).—In reply to Whitby, it is of course known that gelation of rubber solutions can be effected by catalysts, *e.g.*, benzoyl peroxide, in the dark. Although I have never observed such an effect, it seems possible that, given suitable conditions, "rubber peroxide" produced in the early part of the reaction might bring about gelation of the solution on standing for a sufficiently long time in the dark.

In reply to Stevens, it should be realized that speed of gelling in the presence of air is an ambiguous term, since it may or may not include the time taken to absorb the oxygen before gelling commences. The firmness of the gel is a definite property which is always decreased by milling the rubber. Different samples of rubber may give different speeds of gelling, but, after milling, the resulting gel is invariably weaker than that obtained from the same unmilled rubber. The longer the milling, the weaker the resulting gel. It is not clear that the two results quoted by Stevens do not agree with the opening statement of section (e). The bringing into solution of the gel fraction reduced the molecular size, and it is possible that the particular sol fraction had the same average molecular size as the average size of the masticated total rubber.

The quantity of benzophenone used in the experiments with hydroquinone and sulfur was only 1 and not 20 per cent on the rubber. It was essential to use the activator, since the experiments were made in benzene solutions and not in mixed solvents.

I do not agree with Stevens that the properties of dried photogels are unlike those of vulcanized rubber except in high tensile strength, which is a property which is only developed after a considerable degree of vulcanization has been effected.

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- <sup>1</sup> Stevens, *Trans. Inst. Rubber Ind.* 16, 211 (1940).  
<sup>2</sup> Stevens, *Trans. Inst. Rubber Ind.* 16, 223 (1940); Table V.

### $\alpha$ -METHYLENIC REACTIVITY IN OLEFINIC AND POLYOLEFINIC SYSTEMS

ERNEST HAROLD FARMER

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 765-773, October, 1942)

# THE COURSE AND MECHANISM OF AUTOOXIDATION REACTIONS IN OLEFINIC AND POLYOLEFINIC SUBSTANCES, INCLUDING RUBBER

E. H. FARMER, G. F. BLOOMFIELD, A. SUNDRALINGAM  
AND D. A. SUTTON

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 756-764,  
October, 1942)

AND

# IONIC AND RADICAL MECHANISMS IN OLEFINIC SYSTEMS; WITH SPECIAL REFERENCE TO PROCESSES OF DOUBLE-BOND DISPLACEMENT, VULCANIZATION AND PHOTOGELLING

ERNEST HAROLD FARMER

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 774-779,  
October 1942)

## DISCUSSION

J. Weiss (*Newcastle-on-Tyne*).—Farmer's observation as to the formation of peroxides confirms the previous work of Criegee and his collaborators<sup>1</sup>.

This accords with general considerations concerning autooxidation reactions<sup>2</sup>, and the structure of hydrocarbon peroxides and graphitic oxide, as discussed previously<sup>3</sup>. More recently, observations on the reversible quenching of the fluorescence of hydrocarbons by oxygen molecules<sup>4</sup> have made it possible to elucidate the mechanism of the formation of these peroxides. The detailed evidence for the mechanism indicated below will be given in a paper to be published with Weil-Malherbe.

The main point is that the first step consists in an electron transfer from the (unsaturated) hydrocarbon molecule to the oxygen molecule. It is clear also that only hydrocarbons containing  $\pi$ -electrons (double bond electrons, particularly those from conjugated double bonds) have a sufficiently low ionization potential, and in the photochemical reaction this ionization potential is further decreased roughly by an amount corresponding to the (optical) excitation energy of the hydrocarbon molecule.

We then have the following sequence of reactions ( $C_nH_m$  unsaturated hydrocarbon):

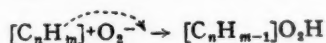
- (1) light absorption  $C_nH_m + h\nu_1 \rightarrow (C_nH_m)^*$  (excited molecule);
- (2) fluorescence emission  $(C_nH_m)^* \rightarrow C_nH_m + h\nu_2$ ;
- (3) quenching by oxygen  $(C_nH_m)^* + O_2 \rightarrow [C_nH_m]^+O_2^-$ .

In the case of reversible quenching this is followed by:

- (4)  $[C_nH_m]^+O_2^- \rightleftharpoons C_nH_m + O_2$ .

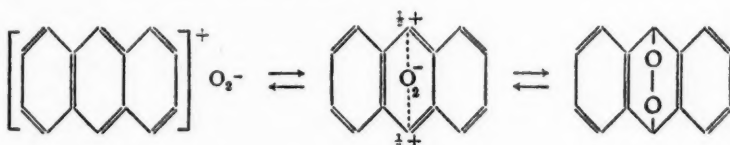
It is, however, possible that the primary (ionic) moloxide formed in reaction (3) will also be stabilized.

In many cases one might expect the migration of a proton from the positive hydrocarbon ion to the negative oxygen ion, so that we obtain:

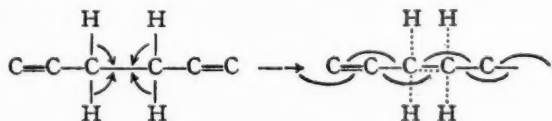


*i.e.*, resulting in the formation of a type of peroxide, as described by Farmer and others.

However, this need not always be the case, and the formation of peroxides in conjugated polycyclic hydrocarbons (anthracene, rubrene, etc.) which have been studied, particularly by Dufraisse<sup>5</sup>, leads to the formation of so-called transannular peroxides, *i.e.*, in these cases no proton migration takes place and the final product of reaction is represented by the general formula  $[C_nH_m]^+O_2^-$ , which is at least partly ionic in character and which is represented by the following structural formulæ in the case of anthracene: (the positive charge is "smeared out" over the whole of the conjugated bond system with a preferential localization on the meso-positions).



L. C. Bateman (*Welwyn Garden City*).—(1) The greater resistance of 1,5-diene systems, compared with 1,4-dienes, to isomerization on heating with alkali may be due to a minor degree of conjugation, which enhances their stability. The partial nonlocalization of the C—H bond electrons is well established in related systems and we may, therefore, write:



This conjugation is not in conflict with the polarizabilities envisaged by Farmer if these are regarded as primarily electromeric, but this agreement does not extend to the explanation of the "cracking" rule of diene polymers, where I do not regard the formal strength of the breaking bond as the sole determinative factor.

(2) Although it is not certain that the same mechanism operates in the thermal autooxidation of solid rubber as in photooxidation in solution, the kinetic scheme of Morgan and Naunton can be brought into harmony with Farmer's results if we redefine their symbols, *i.e.*,  $R^*$  represents a rubber molecule activated at an  $\alpha$ -methylene group;  $RO_2^*$  the first product of oxygen addition—still activated; and  $RO_2$  a normal rubber hydroperoxide. This mechanism is also consistent with my own recent unpublished kinetic data on the photooxidation of solutions of methyl cyclohexene and of rubber.

L. B. Morgan (*Manchester*).—Farmer has marshalled a considerable array of evidence for his contention that initial autooxidation attack on rubber is not on the rubber double bond but on the  $\alpha$ -methylene carbon atom. Naunton and I had suggested that the simplest chain mechanism scheme required to

explain the data then available was, as quoted by Farmer, one involving the entities  $R$ ,  $R^*$ ,  $RO_2^*$  and  $RO_2$ . The general scheme was based on kinetical considerations, but the locality of the place of attack and the nature of the entities involved, could obviously not be deduced from the type of measurements we made, and our reason for assigning the locality of attack as the double bond was because that looked the most likely on the organic chemical views extant at that time.

It is gratifying to find that the more modern organic chemical views advanced by Farmer key in well with our suggested general scheme. The chain propagation reactions suggested by Farmer are, as pointed out by Bateman, identical in form with the propagation reactions set out in our general scheme.

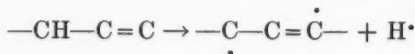
In considering the implications of the zero order of the oxidation with respect to oxygen on the possible mechanism of the process, the complete process should be considered. For example, it is possible to accommodate a bimolecular initiation involving oxygen and hydrocarbon by postulating a bimolecular termination involving oxygen and either  $R^*$  and  $RO_2^*$ . This arrangement also gives a zero order course of oxidation.

The reason why we consider that initiation does not involve oxygen collisions is based not only on the fact that the autooxidation is independent of oxygen pressure but on the fact that initiation by copper or introduction of antioxidant does not result in any change of order of reaction with respect to oxygen. If the zero order with respect to oxygen had been due to oxygen reacting at the same order of reaction in both the initiation and termination steps and consequently cancelling out, then the copper-catalyzed autooxidation should give a rate varying inversely with the oxygen pressure, and the presence of antioxidants should tend to make the rate directly proportional to the oxygen pressure. Actually the observations are that neither addition of copper salts or antioxidants have any effect on the order of the reaction with respect to oxygen. This strongly supports the assumption that neither initiation nor termination of the reaction chains involve oxygen collisions.

In considering the nature of the initiation reaction, it must be borne in mind that the kinetical arguments are based on observations made on vulcanized rubber and not on a pure hydrocarbon. We know that vulcanization not only increases the rate of rubber oxidation but also alters the course the oxidation takes. It is not known whether or not oxidation of raw rubber is independent of oxygen pressure. Therefore it may be possible that either of the initiating reactions suggested by Farmer, *viz.*:



or



occur in a pure rubber hydrocarbon.

In vulcanized rubber it is very likely that the first does not occur, at least to any appreciable extent. The second takes no account of the effect of vulcanization on the oxidation, and it is very likely that vulcanization introduces something into the rubber structure which either takes part in or affects the initiation.

H. S. Lilley (*Slough*).—In his discussion on the addition of maleic anhydride to unsaturated systems, Farmer neglects the published literature on this subject, all of which does not support his theory. Attention should, for instance, be drawn to the survey of this field prepared by Bevan<sup>6</sup>, especially to Section V

of that survey. In this discussion it is pointed out that unsaturation falls as maleic anhydride is added. Attention should be given also to the part played by the carboxyl group in this reaction, since it is known that different results are observed according as maleic anhydride itself, maleic ester or salts of maleic acid are employed. Farmer will find some discussion on this matter in British patent 500,348.

Reference should especially be made to a paper by Bickford<sup>7</sup> on the addition of maleic anhydride to unconjugated fatty acid esters, such as methyl oleate, methyl linoleate and methyl linolenate. In this paper it is pointed out that, in the case of methyl oleate, unsaturation is not affected by the addition of maleic anhydride, but that in the other cases addition is partly at the double bond and partly at activated methylene groups. These observations show the effect of position on the behavior of double bonds and support the contentions which were advanced by Morrell.

Farmer makes no reference to the addition of hypochlorous acid to unsaturated systems, although he himself has worked considerably in this field. Observations which have been made with this reagent do not all support his contentions. Consideration should be given, for instance, to the addition of hypochlorous acid in alcohols and acids as solvents, whereby chloro ethers and chloro esters are obtained. These cases do not seem to fit the former hypothesis and similar considerations seem to apply to the attack of ethyl hypochlorite and other organic hypochlorinating reagents on double bonds.

Farmer makes some mention of the double bond displacements, and refers to the work of Moore and Kass and Burr. It should be pointed out that it has recently been established by Bradley<sup>8</sup> that these changes are certainly reversible in the case of tung oil acids, and it has recently been shown by Denington and the writer that a similar reversibility applies to the case of other doubly unsaturated fatty acids<sup>9</sup>.

Farmer also makes no mention of the case of the addition of hydrogen peroxide to double bonds. The literature of this case is not very clear, but it does not in all cases support action at a methylene group instead of at a double bond.

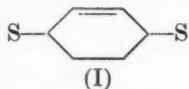
H. P. Stevens (*Beccles*).—E. H. Farmer, in his references to the photogelling of rubber, suggests that fragments of the solvents and/or sensitizers resulting from photolysis react with the rubber. Taking the simplest case of a solvent mixture of hydrocarbon and acetone, the latter according to Norrish would not undergo decomposition from an irradiation of a longer wave-length than 3300 Å.U. As a rubber sol in the solvent mixture gels in a few hours when exposed to sunlight in a glass tube, it seems that gelation takes place under conditions which preclude decomposition of the acetone. I have exposed acetone sealed in a tube free of air for months to direct sunlight without noting any change. I suggest that gelation may result in the first place from a loose combination of the rubber and solvent molecules. I find that the rate of gelation in hydrocarbon solvents is specific to the solvent and appears related to the size of the solvent molecule.

E. H. Farmer (*Welwyn Garden City*).—In reply to Lilley, who has raised a number of interesting points, I would point out that I am well acquainted with the work of Bevan, which in its general results corresponds fairly well with that of Farmer, Bacon, *et al.* on the combination of rubber with maleic anhydride. To elucidate both sets of reactions, the work cited above with cyclohexene and maleic esters was begun. The cyclohexene reactions show some unexpected features, *viz.*, some reduction in acidity of the derived acids and



apparently an undue loss of unsaturation, as are met in Bevan's reactions and in the recent reactions of Bickford between olefinic acids and maleic anhydride. The simplest cyclohexane adduct has the precise constitution shown in the text, and there appears to be little doubt from Bickford's results that an analogous constitution applies to the case of oleic ester, and probably applies generally where only one molecule of the maleic compound is combined with the olefinic compound. The complications set in when two or more molecules of maleic compound are combined. I have made many observations, but have not fully satisfied myself as to whether the anomalies in the case of cyclohexene are due to thermal alteration of the system I ( $S$  = succinic ester grouping), or whether the second molecule (in part) and later molecules of the maleic compound combine in a different way from the first. I agree with Bickford (but not as misquoted by Lilley) that the first molecule of maleic compound reacts rapidly to saturate a double bond, and that the reaction of the second molecule is principally of the same nature, but I cannot yet say definitely whether or not the bond saturated in the second stage is again in the maleic component. Since the reactions occur readily with monoolefins and still more readily with unconjugated polyolefins, any idea that they depend on the occurrence of conjugative isomerization in the olefin prior to Diels-Alder addition must be discarded. Evidence on the subject will be published later.

With respect to hypochlorous acid and its esters, reaction with olefinic substances seems to occur usually by addition at the double bonds. Rubber appears to represent a special case, and other branched-chain polyolefins are probably similar, but recent investigation (unpublished) by G. F. Bloomfield has shown that the reaction of rubber with halogens is less simple than at first appeared to be the case.



Lilley's statement regarding the reversibility of double bond displacement in diene and triene acids, as investigated by Bradley, is misleading. There is no evidence in Bradley's work of the change:

conjugated triene  $\rightarrow$  unconjugated or partly conjugated triene, but only of "loss associated with, or due to, intramolecular or intermolecular additions which result in the creation of a double-unsaturated conjugated component and the formation of polymers"—a very different matter.

Hydrogen peroxide and alkyl peroxides (like peracids) appear ordinarily to attack double bonds and no  $\alpha$ -methylene groups. There is, however, the remarkable ability of hydrogen peroxide (under pressure) to oxidize the  $\gamma$ -methylene group in fatty acids to carbonyl. Concerning the reaction between oil-soluble resins and drying-oils, I regret that this is too large a subject to discuss here.

The concept of the formation of ionic moloxides between olefinic substances and oxygen appears to the authors from their present information to be of doubtful validity. It is especially not obvious how the mechanism described leads to a chain reaction and why the  $\cdot\text{OOH}$  group appears on an  $\alpha$ -carbon atom. The suggestion, however, is an interesting one, and clearly a careful examination of the implications of the hypothesis will be necessary before a final conclusion can be reached.

The suggestion of Stevens that rubber combines loosely with the solvent appears to be unsupported by any experimental evidence and is, in the view



of the authors, unlikely. The further suggestion that light is absorbed by the solvent molecules does not represent the only possibility. Alternatively, light may be absorbed by rubber as in the absence of any activator, but the subsequent reaction with the activator may lead to longer chains or more extensive reaction, or lead to the formation of active radicals. There is not at present any experimental evidence to show which of these possibilities is the correct one.

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<sup>2</sup> Haber, *Naturwissenschaften* **19**, 450 (1931); Weiss, *Nature* **133**, 648 (1934).  
<sup>3</sup> Weiss, *Nature* **145**, 744 (1940).  
<sup>4</sup> Bowen and Williams, *Trans. Faraday Soc.* **35**, 755 (1939); Weil-Malherbe and Weiss, *Nature* **149**, 471 (1942).  
<sup>5</sup> For full references, see Bergmann and McLean, *Chem. Rev.* **28**, 367 (1941).  
<sup>6</sup> Bevan, "Varnish Making", p. 34.  
<sup>7</sup> Bickford, *Oil and Soap* **19**, 23 (1942).  
<sup>8</sup> Bradley, *Ind. Eng. Chem.* **34**, 178 (1942).

## THE STEREOCHEMISTRY OF THE RUBBER MOLECULE

C. W. BUNN

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 704-708, October 1942)

AND

## THE LONG SPACING IN RUBBER

ADOLF SCHALLAMACH

(RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 15, No. 4, pages 780-783, October 1942)

## DISCUSSION

L. R. G. Treloar (*Welwyn Garden City*).—In considering the relation between mechanical properties and molecular structure there are two transitions to be kept in mind: (1) the glassy solid  $\rightarrow$  amorphous rubber transition, which occurs at about  $-67^{\circ}\text{C}$  in raw rubber, and (2) crystalline solid  $\rightarrow$  amorphous rubber transition, which usually occurs at about  $+10^{\circ}\text{C}$ . Transition (1) is not strictly a change in state, but is more correctly a change in internal viscosity, comparable with the hardening of a glass, as the work of Alexandrov and Lazurkin, for example, shows. The temperature of this transition is determined, as Tuckett has shown in his contribution, by the intermolecular forces and by the steric hindrances to rotation in the molecule, although it is not easy to separate these two factors. Transition (2) can take place only when a sufficient degree of regularity exists in the molecule; crystallization is a comparatively slow process, involving relatively large displacements and disentanglements of portions of molecular chains. It does not occur in unstretched rubber below about  $-35^{\circ}\text{C}$ , because there is then insufficient thermal agitation, though the rubber retains its elasticity. It is not surprising that polyethylene, with its simple regularity, crystallizes readily and has a high "melting point", nor that rubber, with its *cis* structure, is more difficult to crystallize than its *trans*-isomer gutta-percha. It is not necessary to sup-

pose, as Bunn does, that this is connected in any significant way with the internal rigidity of the molecule. The fact that amorphous rubber is elastic down to  $-67^{\circ}\text{C}$  proves that the molecules are still flexible at temperatures very much below the crystal melting point; it cannot, therefore, seriously be maintained that differences in internal rigidity (whether due to steric groups or bond orientation effects) can account for differences between crystal melting points of various rubbers amounting to  $100^{\circ}\text{C}$ .

In explanation of the variation of crystal melting point mentioned in the paper, I would like to make the following suggestion.<sup>†</sup> In a normal crystal there are lattice forces tending to hold the atoms in their correct positions, and thermal motion of these atoms tending to remove them. In a rubber there is a second factor tending to disrupt the crystal. This comprises the tensions in the amorphous portions of partially crystallized molecules, in consequence of which the melting point is lower than it would be for a relatively low-molecular compound of the same constitution. When raw rubber is crystallized for a long time, the tensions in the "amorphous" portions of molecules relax, owing to slow molecular rearrangement, and the amount of the amorphous component is reduced, hence the melting point rises with years of crystallization. This explanation accounts for a number of remarkable phenomena connected with the crystallization of rubber. For example, it explains the lack of a sharp melting point, the "local" melting point being determined by the "local" state of tension. It explains why the melting point is lower, the lower the temperature of crystallization<sup>1</sup>, for with lowering of temperature there is a reduction in the molecular relaxation. The retraction of stretched rubber may also be thought of in this way. In vulcanized rubber, internal tensions are high. The crystals formed on stretching "melt" under the action of these internal tensions as soon as the external tension is removed. The higher the state of vulcanization, the higher the internal tensions and the lower the melting point (*cf.* T-50 test for vulcanization)<sup>2</sup>.

Finally, I refer briefly to Bunn's views on the applicability of the kinetic theory of elasticity to rubberlike materials, as expressed in his recent papers.<sup>3</sup> If I have understood him correctly, he does not accept the theory in the form developed by Kuhn, but refers to a modified kinetic theory of Bresler and Frenkel, involving restricted rotation about single bonds. I should like to point out that Bresler and Frenkel's theory requires that the tension in stretched rubber should vary as  $T^2$ , a result which does not accord with the experimental evidence, as will be seen from the paper which I have submitted to this discussion.

W. T. Astbury (*Leeds*).—I have had the feeling throughout much of this general discussion that not enough recognition is being given to the fact that elastic high polymers are aggregates of molecules. There are interactions not merely between parts of the same molecule, but also between neighboring molecules. It is not enough to isolate chains in the mind and then to apply thermodynamic or similar reasoning to see whether these chains can or can not coil; it is necessary to know also what neighboring chains have to say about it. They may not care a great deal—but on the other hand they may. The extended chain-molecules may fit together readily side by side, or they may be very awkward partners, quite apart from the question of how easily they may coil up as individuals. Thus it is not inconceivable that, whether or not rubber possesses greater intramolecular facilities for coiling than gutta-percha does, the extended molecules of the latter may form regular crystallites more easily in any case: and similarly, though the chains of polyethylene appear

to have considerable potentialities for coiling and, therefore, might be expected to show long-range elasticity also at lower temperatures, it is perhaps not a matter for surprise that they do not, when we remember the excellent crystal structures formed by the shorter chain paraffins. The average size and the perfection of the crystalline aggregates must count, too, in deciding the "melting point" or onset of long-range elasticity, and the gradual rise of the "melting point" of rubber on standing might be due only to increasing intermolecular organization without introducing cross-linkages.

G. A. Jeffrey (*Welwyn Garden City*).—Bunn has referred to his crystal structure analysis of rubber. The picture of the rubber molecule he has derived from that analysis is based on experimental evidence consisting of spacing measurements and visual intensity estimations of some forty spots. Of these forty spots, only eight can be assigned to individual crystal planes; the remainder are composed of reflections from two and often more planes. Whereas these measurements may be adequate for the selection of a unit cell and space group, depending on the accuracy with which they could be made, the data are certainly not sufficient for the complete structure analysis that is claimed.

There are ten atoms in the diisoprene repeating unit, and there are thirty parameters to be determined. The x-ray intensity for any general plane is related to the square of its structure factor, which is calculated from a trigonometrical equation of thirty variables. If it is assumed that the rubber molecule possesses the normal bond lengths of 1.54 and 1.34 Å.U. for singly and doubly bound carbon atoms with tetrahedral valency angles, then the parameters are not independently variable, and the number of combinations that satisfy the observed intensities may be quite small and there may possibly be only one solution. If, however, these standard distances and angles are disregarded in efforts to satisfy the observations, then there will be an immense number of combinations of parameters to be considered, quite beyond the possibility of calculations, and with the very limited experimental data available from the rubber fibre diagrams there are probably many solutions. Bunn's crystal structure of rubber with its unusual valency angles and single bond distances varying between 1.49 and 1.56 Å.U. is one of these combinations. An average experimental error of  $\pm 0.05$  Å.U. is now quoted for the atomic coördinates, and this would cover a number of the abnormal values. But if the atoms are adjusted within that error to fit a less distorted molecule, then much of the qualitative agreement between the observed and calculated intensities is lost, and it is concluded that these distortions must be regarded as significant if this solution to the structure is accepted. There is no evidence that it is the only or even the most likely solution, and its validity, depends, therefore, on the justification of the following original features:

- (1) distortion of the methyl groups  $15^\circ$  and  $35^\circ$  out of the ethylenic valency plane;
- (2) two isoprene units undergoing different distortions;
- (3) unusual interatomic distances and valency angles.

With regard to distortions, the strongest known intermolecular forces in crystals are hydroxyl bonds, and in the analyses of structures in which these occur there have never been found any interatomic discrepancies in any way comparable with these proposed for rubber.<sup>4</sup>

The only examples of abnormal intercarbon distances are in those molecules where resonance occurs between several electronic states.

The structure analysis by direct adjustment of parameters to fit visual intensity estimations may lead to erroneous conclusions. Some account of the limitations and precautions necessary for the application of this method is contained in a paper on the crystal structure of melamine.<sup>5</sup> Examples are known where trial and error calculations have suggested structures which have subsequently been disproved by the more precise methods of Fourier series with quantitative absolute intensity measurements.<sup>6</sup>

In these investigations the number of parameters was much less, and the experimental data were much more than for crystalline rubber, and the chances of ambiguity in the analysis of rubber can be assessed accordingly. In my opinion, the evidence is insufficient to support this structure advanced by Bunn.

W. J. C. Orr (*Welwyn Garden City*).—In addition to the difficulty, just mentioned by Jeffrey, of determining atomic positions in the lattice cell when normal bond distances and angles have been disregarded, it is necessary to enquire also whether the extra van der Waals' interactions which result from crystallization can supply all the energy involved in these distortions and give, in addition, the surplus of 400 to 500 calories per  $C_5H_8$  unit, which is the observed experimental heat of crystallization of rubber. (One assumes, in the absence of evidence to the contrary, that unstretched rubber has normal bond and angle parameters.) If one allows a tolerance of  $\pm 0.01$  Å.U. on all bond distances, and  $\pm 5^\circ$  on all angle parameters, it may readily be calculated, using, for example, the force constant data of Wilson and Wells<sup>7</sup>, that to produce these deviations (above these tolerance limits) involved in Bunn's crystal structure would require about 4400 calories per  $C_5H_8$  unit, of which 3750 calories would be required for the angle distortions and 650 calories for the bond distortions. This would imply that the small increase in density and the improved coördination resulting from crystallization would require to produce about 4800 calories per  $C_5H_8$  unit, whereas from one's present knowledge of the magnitude and range of these van der Waals' forces one would not expect to obtain more than about 400 calories.

In consequence I am forced to the conclusion, contrary to Bunn's findings, that the bond and angle parameters in the rubber crystal must be substantially normal.

J. R. S. Waring (*Manchester*).—Without entering the controversy on the question of x-ray data, which is a specialized field, there is one point in Bunn's paper which is of general interest—where he refers to the melting point of rubberlike substances.

Here is a further example of a state of affairs which has been very noticeable in the discussion to-day—the inability of our current rigid concepts and categories—solids, liquids, melting points—to stand up to the question of rubber. Let us face facts and realize clearly that rubber is a transition state—balanced between solid and liquid, and we can bring out the solid or liquid aspects of this material by altering the time factor element in the experiments we perform. Slow processes like swelling, diffusion—as indicated so well in some papers—emphasize the purely liquid character—fast alternations of stress bring out the solid nature of this material.

If we discuss melting points, would it not be more accurate to view this question from the standpoint of a melting range, and specify in every detail the previous history of the sample. For example, I know of at least one sample of polychloroprene which was quite rubbery at room temperature, but which became frozen when stretched to less than 100 per cent elongation for

some days at room temperature. No recovery was observed after removal of stress, and x-rays showed the material to be crystalline. On warming, recovery was complete and fairly sharp at about 30° C. Further elucidation of the question of melting range should be possible by linking up experiments on "freezing" and "melting" with a theoretical distribution of relaxation times—associated with different molecular types.

C. W. Bunn.—The criticisms of Jeffrey and Orr on the details of my proposed structure of the rubber crystal are based on a misunderstanding. They are evidently referring to Figure 7 of my original paper<sup>8</sup>, in which bond lengths and angles differing from the normal values are marked. But these figures were given, not to claim an accuracy of 0.01 Å.U., but rather as a frank demonstration of the sort of experimental error one may expect in work of this sort. I am sorry if that was not clear; but it is stated plainly in that paper, and again in the present communication, that while the general geometry of the molecules and their arrangement in the crystal are presented with considerable confidence, the actual atomic coördinates must be regarded as only approximate. It would be unreasonable to claim more than this, and I have not done so. The bond lengths and angles in the rubber crystal may well be normal.

There are, however, two distortions which are too large to be accounted for by experimental errors and which are, therefore, probably genuine: (1) The two isoprene units in the crystallographic repeating unit differ in configuration, chiefly in the orientation of the CH<sub>2</sub>—CH<sub>2</sub> bonds. Now there is nothing improbable about this; it is simply a question of rotation round single bonds to different degrees in the two cases—a rotation which involves only a small amount of energy. Moreover, such a difference between successive chemical repeating units is formally analogous to the differences between crystallographically different molecules in certain well-established structures; in transazobenzene, for instance, half the molecules are almost exactly flat, while in the others the benzene rings are rotated some 15° about the C—N link<sup>9</sup>. Such distortions appear to be due to the packing together of awkwardly shaped molecules. In the rubber structure, this difference between successive isoprene units is adequately explained on this basis; inspection of a model shows that this distortion is just what would be expected on account of packing difficulties. (2) The methyl groups do not lie in the ethylenic valency plane. This sort of distortion is found in the three related structures, *β*-gutta-percha, rubber and polychloroprene; in each case the x-ray intensities demand it. The magnitudes as determined by interpretation of the x-ray intensities may be rather approximate, but the effect does seem to be real. This distortion is an intramolecular effect, and appears to be due to repulsion of the methyl group by a chain CH<sub>2</sub> group lying on one side of the ethylenic valency plane; if, by rotation round the C—CH<sub>2</sub> bond, the pressure on the methyl group were relieved, then the CH<sub>2</sub> group in question would then be too close to the CH group. Perhaps

a simpler way of regarding it is this: if, in the group  $\text{CH}_2\text{—CH}_2\text{—C}$ ,  
 $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH} \end{array}$   
 the angle CH<sub>2</sub>(1)—CH<sub>2</sub>(2)—C is to remain approximately the tetrahedral angle,

then the distances CH<sub>2</sub>(1) to CH<sub>3</sub> and CH<sub>2</sub>(1) to CH are bound to be smaller than the sums of the usual external radii of these groups, if the ethylenic group remains flat; the distortion of this group to a slightly pyramidal form is pre-



sumably the result of a compromise between the various forces involved. By rotation round the bond  $\text{CH}_2(2)-\text{C}$ , the pressure on either  $\text{CH}$  or  $\text{CH}_3$  can be relieved, but only at the expense of increasing the pressure on the other; consequently, whatever the position of  $\text{CH}_2(1)$ , the ethylenic group is likely to be slightly pyramidal.

With regard to the suggestion that there may be alternate structures for rubber which would fit the x-ray patterns as well as the one I have proposed, I can say only that anyone who attempts crystal structure determination must be prepared for such possibilities, that I had this in mind when I was trying to solve the rubber structure, but that I have not been able to find an alternative. I cannot say there is no other possible structure—the problem is too complex to permit such a statement; but I have not been able to find one.

Let us try to maintain the correct perspective with regard to the interpretation of x-ray photographs of high polymers. Work on simple polymers such as rubber and synthetic polymers lies somewhere between the precision work on single crystals composed of small molecules (exemplified in the work of J. M. Robertson on benzene derivatives, for instance) and the suggestive and speculative work on complex natural polymers (exemplified in the work of Astbury on the fibrous proteins). In the former, a high degree of certainty with regard to the whole arrangement, and a high degree of precision of atomic coördinates, are attainable, owing to the large amount of information on single-crystal diffraction photographs and the not-too-complex structures of the molecules so far studied. In the latter, owing to the complexity of the molecules and the limited experimental data, it has not yet proved possible to solve structures completely, or even to be very sure about unit cell dimensions; but consideration of certain spacings, particularly the repeat distance along the chain molecules, has led to suggestions of the greatest value with regard to molecular structure. For simple polymers, the possibilities lie between those extremes; in spite of the limited experimental data contained in the familiar fibre photographs, it has proved possible to determine unit-cell dimensions and even approximate atomic positions with, I believe, a fair degree of certainty. We must not expect the same degree of certainty as in single-crystal work; but this need not, and should not, deter us from seeking complete solutions.

The adventure has its risks, but if we are to advance our knowledge of polymer structures and our understanding of the physical properties of these substances in terms of molecular physics, these risks must be taken. Let us accept them boldly, for the possible prizes are well worth the risks. We need not fear being led astray for very long, for each new structure determined with fair certainty will provide checks on, and will itself be counter-checked by, previously determined structures, and our confidence in each separate structure will increase with the growth of a consistent body of knowledge; any structure which is not consistent with others, particularly those of closely related substances, will be reconsidered.

Now, as far as we have gone up to the present, my suggested structure for the rubber crystal survives such a test very well. The three related structures— $\beta$ -gutta-percha, rubber and polychloroprene—hang together very well; the molecules are found to be built on similar principles. It is very significant that interpretation of the three very different x-ray diffraction patterns of these three substances has led to structures which are consistent with each other; if we associate each one separately with a given probability of correctness, the fact that they are consistent with each other very much increases our confidence in each.



Now a word about methods of solving polymer structures. Fourier series methods have been mentioned; but it is unfortunately not generally possible to use them for polymer structures. I have used them myself for the simplest of all polymer structures, that of polyethylene<sup>10</sup>, but this is likely to remain an isolated example, for in more complex examples the overlapping of reflections bars any attempt to use such methods. There is no escape from the hard fact that most polymer structures must be solved by trial-and-error methods, unless a method of growing single crystals of such materials is discovered. Before leaving the subject I should like to say that, as I see it, the Fourier series method, when it can be used, is not necessarily superior to or more certain than trial-and-error procedure, except in very special circumstances. For instance, if there are two arrangements of atoms, both satisfying the observed intensities, then there are two different electron density maps obtainable by assigning different sets of phase angles to the various terms of the Fourier series. The advantage of the Fourier method is that it is a more direct way of adjusting parameters. But it is well recognized that the final test of any structure (apart from the comparison with related structures) is a good overall agreement between observed and calculated intensities<sup>11</sup>. It does not matter how this agreement is attained—whether by rigid deduction from the x-ray pattern alone (using either Fourier synthesis or trial-and-error methods or, as is more usual, a mixture of the two), by reasonable induction from general principles arising from a survey of previously determined structures, by intuition, or even by sheer guess-work.

With regard to the various remarks on the melting point of rubber, the lack of sharpness of melting point is shown by other polymers than rubber, and is probably a quite general phenomenon among crystallizable polymers and is, I believe with Treloar, due to "the tensions in the amorphous portions of partially crystallized molecules". The suggestion, made by both Astbury and Treloar, of continued slow crystallization over a long period of time, is a welcome contribution to the problem of the dependence of the melting point of rubber on its past history and of the phenomenon in polychloroprene mentioned by Waring.

I agree with Astbury and Treloar that difficulties of packing may play some part in determining the melting point of a polymer crystal, but I doubt whether this effect is serious in the substances mentioned. The efficiency of packing is indicated by the density of the crystal, and the densities of rubber,  $\beta$ -gutta-percha and polyethylene crystals are very closely similar (see Part 3 of my paper<sup>8</sup>). Good packing does not depend on molecular symmetry; it is possible to imagine highly symmetrical molecules which would pack badly, and quite asymmetric molecules which would pack very well. (To take a two-dimensional analogy, the pieces of a jig-saw puzzle fit together perfectly even when quite asymmetric; and in three dimensions, consider the fact that regular octahedra do not pack together to fill space while triclinic parallelepipeds do).

Astbury has drawn attention to the fact that shorter-chained paraffins crystallize well, just as polyethylene does. This is a very fruitful line of approach; I believe we can learn a lot about the melting points of high polymers from existing knowledge on the melting-points of their shorter-chained analogues.

With regard to Treloar's first paragraph, I would say that the melting point of a polymer is the result of a balance of forces. Melting occurs when the coöperative intermolecular forces making for crystallization are just balanced by the lateral thermal movements which depend on molecular flexibility.

If, for any reason, crystallization is prevented—as in interpolymers of irregular molecular structure, or when a regular polymer such as rubber is cooled rapidly so that molecules do not have a chance of getting into the right positions (in other words, the intermolecular forces are not given a chance to coöperate)—then the molecules will be able to wriggle at a temperature far below the equilibrium melting point. The action of plasticizers can be explained in the same way.

On the kinetic theory of elasticity, I would say that Mark's fundamental suggestion still holds the field as a general concept; there seems no alternative. But Bresler and Frenkel's criticism of the extreme form of the theory developed by Kuhn does seem to me sound. There is little reason to doubt that there is a potential barrier to rotation round the single bonds in the rubber molecule; consequently, if the acceptance of this leads to wrong results (for the variation of tension with temperature, and for the magnitude of the modulus of elasticity), then surely this means that some other factor (hitherto neglected) must play a part. This was, in fact, the main conclusion of Bresler and Frenkel's paper, and they suggest that molecular interaction is the other factor—or, perhaps, one should say, one of the other factors. The suggestion seems to me a reasonable one; molecular interaction is important in everything except perfect gases, and in a substance having a density of nearly 1, it must be very important indeed.

May I conclude, in reference to Waring's remarks, by reiterating that the problem of rubberlike elasticity is the problem of the mechanical properties of very long-chain polymers above their melting points. Polymers which are rubberlike at room temperature are simply polymers which have melting points below room temperature. Rubberlike substances are, from the physico-chemical point of view, liquids—a special type of liquids owing their coherence primarily to the great length of their molecules and secondarily to any cross-linking we may be able to effect.

#### REFERENCES

- <sup>1</sup> I find that the following concept has been elaborated by Alfrey and Mark (cf. *J. Phys. Chem.* **46**, 112 (1942)).
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- <sup>3</sup> *Ind. Eng. Chem., Anal. Ed.* **5**, 279 (1933).
- <sup>4</sup> Bunn, *Proc. Roy. Soc.*, **1942**.
- <sup>5</sup> Cf. pentaerythritol (Llewellyn, Cox and Goodwin, *J. Chem. Soc.* **1937**, 883); polyvinyl alcohol (Mooney, *J. Am. Chem. Soc.* **63**, 2828 (1941)).
- <sup>6</sup> Hughes, *J. Am. Chem. Soc.* **63**, 1737 (1941).
- <sup>7</sup> Robertson, *Ann. Rept.* **1931**, p. 180.
- <sup>8</sup> Wilson and Wells, *J. Chem. Physics* **9**, i, 319 (1941).
- <sup>9</sup> Bunn, *Proc. Roy. Soc.* **A180**, 40 (1942).
- <sup>10</sup> De Lange, Robertson and Woodward, *Proc. Roy. Soc.* **A171**, 398 (1939).
- <sup>11</sup> Bunn, *Trans. Faraday Soc.* **35**, 482 (1939).
- <sup>12</sup> Cox, *Chem. Soc. Ann. Reports*, **1938**.

## RUBBER PHOTOGELS. II.\*

HENRY P. STEVENS

In a previous communication<sup>1</sup> the writer has shown that the formation of gels from rubber sols on irradiation is often accompanied by an increase in weight so that the solvent and (or) sensitizer apparently reacts photochemically with the solute. The increase in weight of the rubber after removal of the solvent was found to be greater the more rapid the gelation of the sol. It was suggested that this increase in weight might result from products formed by reaction between the solvent and sensitizers independently of the rubber; the product in that case might be rubber physically associated with such photochemical products. This seemed unlikely, as prolonged extraction of the moist or dried photogels with acetone and alcoholic potash removed only a part of the increase. As a further check, a mixture of solvents and sensitizers without rubber was irradiated in sealed tubes and the products were examined. These experiments have been repeated by exposure to sunlight in a window with southern aspect for a whole year. In some cases small quantities of non-volatile substances were obtained, but these were readily soluble in acetone and, therefore, did not account for the increase in weight, or at least for only a small part of it, and that part was acetone-soluble.

It appears, therefore, that any reaction which takes place on insolation between the solvents, with or without additional sensitizers, cannot account for the observed increase in weight of dried photogels. The conclusion is reached that a photosynthesis has taken place, and that the gels consist of a rubber reaction product, at least where an increase in weight takes place.

*The anomalous behavior of benzoquinone.*—Every aldehyde, ketone and quinone that has been tried has been found to act as a sensitizer and to promote the formation of a photogel with the one exception of benzoquinone. This is the more surprising since analogous substances such as 1,4-naphthoquinone, anthraquinone and chloranil are all effective gelling agents. As the quantity of sensitizer usually required is substantial, it seemed possible that different results might be obtained with smaller proportions.

The contents of these tubes, after evaporation of the solvent, were subjected to swelling tests which, with times taken to form gels and with yields, are given in Table 1.

The figures are in accord with the conditions of the experiments; when the retarding action is small, some increase in yield is registered. There is also slight solubility and moderate swelling. With inert solvents there is no increase in yield, solubility is appreciable and the swelling index is high. Except for its retarding action, benzoquinone has no apparent influence on the gel formed. Although 1,4-naphthaquinone and chloranil act as sensitizers in promoting gelation, it has been noted that prolonged insolation of the gels *in vacuo* results in these gels liquefying.

It has been previously noted<sup>2</sup> that no obvious relationship exists between

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the figures for proportion soluble and swelling index. It may be that the significance of the latter figure is masked by a part of the rubber having dissolved. It would appear more reasonable to compare the volume of the swollen gels with the weight of rubber contained in them, rather than with the weight of rubber originally taken. A third column, headed "swelling index corrected", has therefore been added to express the swelling capacity of the rubber after making an allowance for that part which has been dissolved.

*Insolation of dry rubber.*—Statements have appeared<sup>3</sup> recording a spontaneous change in solubility of sol rubber fractions. Staudinger<sup>4</sup> has summoned up his experimental evidence as follows. Unvulcanized rubber is transformed on standing into insoluble rubber. This insoluble rubber can be converted into a soluble form by long standing or by mastication. Specimens of pure rubber, prepared with the careful exclusion of air, remain soluble and do not change on long standing if air and light are excluded. But if a small amount of air is admitted, the rubber is slowly converted into the insoluble form.

TABLE I

Solvent	Benzo-quinone (per cent)	Time taken to gel (days)	Yields (per cent)	Proportion soluble	Swelling index	Swelling index (corrected)
(1) Ligroin	1	..	98	1.00	$\alpha$	$\alpha$
(2) Ligroin	0.1	80	97.2	0.22	37	47
(3) Benzene	1	..	101	0.56	41	93
(4) Benzene	0.1	80	98.6	0.39	34	56
(5) Carbon tetrachloride	1	16	110	0.05	15	16
(6) Carbon tetrachloride	0.1	6	116	0.07	15	16
(7) Carbon tetrachloride	Nil	5	130	0.19	14	17

The first two statements put together imply that rubber on standing is transformed to an insoluble modification which, given time, changes back again to the soluble form. There are no records that crude raw rubber undergoes these changes, but they would not be observed in the factory if, as Staudinger states, reconversion to a soluble form takes place on mastication. The next sentences indicate that the change to the insoluble form, at least in the case of pure rubber, does not take place if air and light are excluded, otherwise insoluble rubber is formed. The formation of photogels implies the rendering insoluble of the previously soluble rubber. Being a highly lyophilic colloid, the insoluble hydrocarbon does not separate as a precipitate but forms a gel which, on further irradiation, becomes less solved, the gel contracting and expelling a part of the solvent. As this change takes place slowly, even in the absence of added sensitizers or active solvents, it seemed likely that irradiation without solvent would have a similar effect. A number of small pieces of various raw rubber diffusion fractions were placed in test-tubes open to the air and irradiated by exposure in the window over a period of approximately one year. The rubber fractions had been prepared two or three years previously and filed in envelopes. They had, therefore, been preserved in darkness but in contact with air. No tendency to become insoluble had been noted and, on retesting, all of them were found to disperse readily in benzene in darkness in a day or two. That is, the dispersion properties of the rubber fractions had remained substantially unchanged since they were made.

On the other hand, all specimens which had been exposed to light had become partially insoluble. Judged by solubility and swelling tests carried

out in the manner originally proposed by Spence and Ferry, as in Table 1, they were quite as insoluble in benzene as are many dried photogels. The following figures were obtained, and may be compared with those of the previous publication<sup>5</sup>.

The figures obtained with different specimens vary little between themselves, indicating much the same effect as a result of exposure to sunlight, whatever the solvent originally used for separating the fractions (see Table 2).

These products of insolation of dry rubber do not show appreciable difference on handling from the specimens before insolation, except for a tendency to surface changes, generally adhesiveness. Exposed for a few days at 0°C or below, the specimens showed no signs of stiffening, and remained clear and transparent. Exposure to sunlight in the presence of air has, therefore, altered the constitution in such a way that the specimens are no longer soluble, nor do they freeze. Nor do they show any indication of improvement in physical properties. They are soft, easily pulled into pieces between the fingers, and adhesive at the severed surfaces. In general the insolated specimens

TABLE 2

	Proportion of rubber sol in 10 days	Swelling index	Swelling index (corrected)
(1) 2nd sol fraction from smoked sheet obtained with benzene	0.35	14	22
(2) The same as (1), but obtained with ligroin	0.34	17	26
(3) The same as (1) and (2), but obtained with ethyl ether	0.37	12	19
(4) Benzene diffusion rubber	0.30	17	25
(5) The same as (4), but obtained with a mixture of two parts benzene and one part acetone	0.32	11	16
(6) The same as (4) and (5), but with a mixture of two parts carbon tetrachloride and one part acetone	0.29	14	20

have the properties of photogels after evaporation of solvent, and the effect of insolation of the dry rubber appears to correspond closely to that of a dried gel from a nonreactive liquid such as benzene or ligroin.

In a further series of experiments, a number of specimens were insolated as before, with duplicates in sealed tubes from which the air was removed by adding a few drops of ligroin and boiling off under reduced pressure. Both in air and *in vacuo* a reduction in solubility and in swelling index were obtained. Whereas the original rubbers were either entirely dissolved or yielded voluminous jellies which could be separated from the surrounding benzene with great difficulty and then incompletely, the insolated specimens gave in most cases well defined compact jellies from which the supernatant benzene could be cleanly drained. Some figures are given in Table 3.

There is a marked difference in the surface qualities of the specimens insolated in air and *in vacuo*; the former are soft and sticky and after a long period may show cracks and hardening (resinification), like perished raw rubber.

The figures are for specimens insolated side by side for the same period, and protected by glass. Longer exposure results in further change. A piece of the milled, sheeted crepe rubber, nailed to a board and exposed for a few weeks without glass protection, gave a figure of only 0.25 for proportion soluble and 17.4 for the corrected swelling index. The solubility of this sample in a large range of solvents varied from 0.25 to 0.18. The specimen swelled like



a well vulcanized soft rubber, but its physical properties were hardly better than the starting material.

Tensile figures give breaking loads of the order of 2 per cent of properly vulcanized rubber. Yet if the swelling properties are compared, it is found that the insulated rubber swells to less than twice the volume of the vulcanized rubber under like conditions. The tensile figures and swelling capacity of insulated rubber are quite out of proportion when contrasted with vulcanized rubber.

*Rate of gel formation. A correction.*—It was previously shown<sup>12</sup> that, in the presence of a little air, milling rubber had little or no effect on the rate of gelling<sup>6</sup>. The unmilled rubber lost viscosity before beginning to gel. This and other experiments appeared to indicate that the molecular complexity, that is, the length of the rubber molecule, had little influence on the rate of gelling, although some purified rubber and diffusion fractions gelled more slowly than milled rubber<sup>7</sup>. Further experiments have now been made in which the air was excluded as completely as possible. Although it cannot

TABLE 3

	Proportion in air	Soluble in vacuo	Swelling index (corrected)	
			in air	in vacuo
Milled, sheeted crepe rubber	0.38	0.43	41.7	59.3
Air-dried crepe rubber	0.62	0.17	40.6	26.8
Air-dried crepe rubber from purified latex (LAC. 81)	0.39	0.10	36.8	18.1
Air-dried crepe rubber. Another sample from purified latex (LAC. 80)	0.42	0.18	32.4	28.9
Rubber from NaOH-treated latex	0.65	0.53	43.1	33.3
Ligroin-diffusion rubber fraction	0.30	0.47	17.8	31.0

be assumed that no oxygen was present, the amount must have been small. These experiments show that the molecular complexity is not without effect, as well milled rubber is now found to gel more slowly than rubber broken down only sufficiently to be plastic, and this again gelled more slowly than the original crepe from which it was made.

But the rate of gelling varies appreciably with raw rubbers of different origin, and a milled rubber may gel faster than another before milling. Also the relative order of gelling of a number of specimens is the same in different solvents. Exhaustive acetone extraction has no effect on rate of gelling, as shown in a duplicate series of different specimens, the order of gelling being the same in both series. Although a clot of gel forms rapidly near the surface of sols prepared from dried latex films, the remainder of the liquid remains fluid indefinitely. The clot is dense, and it would seem that so large a proportion of the rubber is withdrawn from solution that the remaining sol is too weak to gel. The occurrence can be misleading if the usual test for gelling is applied, namely, loss of fluidity as indicated by inverting the tube. As originally discovered by Spence<sup>8</sup>, Spence and Kratz<sup>9</sup>, Bary<sup>10</sup>, and Kemp and Peters<sup>11</sup>, only part of a specimen of unmilled raw rubber is capable of dispersion in a solvent, the amount depending on the quality or method of preparation of the rubber and the particular solvent chosen. No solvent is capable of extracting the whole of the hydrocarbon leaving the bare protein scales free from hydrocarbon, even when the treatment be repeated several times over long intervals, with fresh solvent. Hence a solution of unmilled rubber in a solvent, in spite



of repeated shaking, must consist of rubber molecules of relatively low molecular weight fully dispersed, and a generally smaller incompletely dispersed part which forms gelatinous clots suspended in the solution. These relatively coarse particles, prepared from films of evaporated latex and some specimens of crepe rubber, are clearly visible in certain solvents of suitable refractive index. The little flakes of swollen but undispersed rubber are readily visible in ligroin, less so in carbon tetrachloride, but invisible in benzene, although their presence in the latter is often revealed by small clots remaining on the sides of the tube after vigorous shaking. But however violent and prolonged the agitation, these clots remain undispersed if the rubber be unmilled and this may account for the local formation of large clots of dense gel on insolation while the bulk of the liquid containing the more soluble rubber remains unchanged.

Sols in toluene and cyclohexane gel more slowly than those in ligroin. Indications of gelling have been obtained with cyclohexene but not in xylene, tetralin or decalin.

#### DISCUSSION

Having regard to the invariable partial solubility of a rubber insolated without solvents, failure to gel must result from either the presence of an inhibitor, the solubility of the gel in the solvent or the excessive absorption of active rays by the solvent itself. The latter seems unlikely, as gels form in benzene relatively quickly. Nor does the explanation lie in solubility, for experiments made on the solubility and swelling of a series of hydrocarbons with the same photogel formed by insolation of milled sheeted rubber showed that the solubilities were of the same order. This leads to the conclusion that the varying behavior of hydrocarbons results from the chemical nature of these, or from impurities contained in them.

The relative insolubility of raw rubber brought about by insolation introduces a new fact which necessitates a revision and considerable modification of the views expressed in the previous publication. It seems clear that separation of a photogel from a rubber sol is the direct result of the formation of an insoluble type or modification of the rubber, independent of the solvent. It cannot, therefore, be ascribed to a reaction involving cross-linking or any type of combination between rubber and solvent. On the other hand, a reaction may subsequently ensue, promoted by a solvent or sensitizer, or the latter as a negative catalyst may prevent the separation of a photogel, or eventually disperse one already formed.

Previous determination of changes in the weight of the rubber on gel formation enabled a distinction to be drawn between active and inactive solvents, the latter comprising hydrocarbons such as ligroin and benzene, to which may now be added toluene and cyclohexane. Photogels, formed in these hydrocarbons are generally of rather a tenuous consistency, readily revert to sol form on exposure to light and air, and show a small loss of 2 or 3 per cent in weight after drying, as a result of conversion to gel. In such cases it would seem that there is nothing more than separation of rubber rendered insoluble by insolation.

On the other hand, with an active solvent such as carbon tetrachloride or one containing a sensitizer such as a benzene acetone mixture, a reaction proceeds, independently of and simultaneously with the formation of insoluble rubber, and a new rubber derivative is formed, in which molecules of the

solvents react, probably additively with the unsaturated hydrocarbon. No other explanation is possible to account for the large increase in weight of nearly one hundred per cent, or the considerable halogen content where a halogenated solvent is used. The various other possibilities were referred to in the previous communication and a repetition with elaborations has confirmed the previous conclusion that this increase in weight and halogen content cannot be explained on the basis of a reaction in which the rubber does not take part.

The tenuous gels formed in inert solvents which are sensitive to oxidation may be polymerization products, but the tougher products formed with sensitizers consist of rubber reaction products; and these are hardly affected by exposure to air. The former therefore comprise a loose bond readily broken by the addition of oxygen, whereas the latter consist of a relatively stable reaction or addition product, comparable with the hydrochloride. In neither case can the majority of gels be regarded as vulcanization products. If changes such as are measured by solubility, swelling capacity and reduced sensitivity to cold and heat are to be regarded as evidence of vulcanization, independently of improved physical properties, particularly tensile strength, elongation, modulus and recovery (hysteresis), then all rubber products, including the hydrochloride, cyclized rubber, and even hydrogenized rubber, must be regarded as varieties of vulcanized rubber. In a vulcanized rubber, one expects improvement in tensile properties to progress concurrently with resistance to swelling and other characters. This is not the case with insolated rubber.

Neither the product of the insolation of dry rubber nor those obtained by drying photogels can be regarded as improved physically in the manner characteristic of pure vulcanized rubber. The former, or those slowly formed from photogels in inert solvents, are weak, rather adhesive and plastic, generally indistinguishable from the original. Those obtained by longer insolation and with sensitizers are harder and tougher, but their tensile properties are of a lower order than those of properly vulcanized rubber, and they show slow and imperfect recovery after stretching.

Conclusions are best drawn from tests on milled sheeted rubber. Improvements are then readily apparent. If, on the contrary, one starts with unmilled specimens, particularly latex films, comparative improvements are not so obvious, owing to the relatively high tensile properties of the raw rubber itself. If the reactions responsible for the formation of photogels were a matter of oxygen-bridging like sulfur-bridging in vulcanized rubber, one would expect similar enhanced tensile properties. It is known that rubber vulcanized by heat with benzoyl peroxide, which may be supposed to be a matter of oxygen-linking of this type, does lead to such enhanced tensile properties, and these are of the same order as those brought about by the sulfur linking. Photogels of the tenuous sort, if indeed formed by oxygen-bridging, must therefore contain an extraordinarily small number of molecules so bound. Such a viewpoint is perhaps justified in the present state of knowledge, that is, until it has been shown that no reduction in solubility and other characteristics results on the irradiation of rubber in the entire absence of oxygen. Alternatively, the formation of insoluble rubber may be a result of cyclization. As is known, cyclization is brought about by heat, and it is not improbable that the same reaction should result from the action of light. It is also not impossible that the solvent hydrocarbon adds on as a whole to the unsaturated rubber molecules. The attachment of such large groups would tend to immobilize the molecules and decrease solubility. The larger the group the less tendency to

combine; consequently gels would tend to form in benzene more quickly than in toluene, and this again more quickly than in xylene. Such is actually the case. It would explain also the failure to obtain gels in solvents with such large molecules as tetralin and decalin. Acetone and carbon tetrachloride were unchanged when insolated in sealed tubes in the absence of air. Had a reaction ensued, carbon monoxide and ethane would have been liberated in quantity, and the tubes would have burst. Therefore insolation does not provide sufficient energy to break down the ketone or tetrachloride as would artificial irradiation, and it does not appear likely that photogels are addition products in which the double bonds are saturated, say, with methyl groups which would result from the photolysis of acetone. The writer is indebted to Professor R. G. A. Norrish for his interest and to R. R. Smith for carrying out an irradiation test with a mercury-vapor lamp of rubber sols in benzene and tetrachloride under the same conditions as for the photolysis of ketones. The rate of gelling in carbon tetrachloride was of the same order as that in a similar tube exposed to sunlight, that is, 8 hours, compared with 12 hours in sunlight. No gelling took place in the benzene sol in 40 hours. A similar tube took 68 hours in sunlight. Allowance must be made for the fact that the sols were all enclosed in thin-walled glass tubes; nevertheless the experiments seem to indicate that much longer wavelengths suffice for the formation of photogels than for the more drastic photolysis of ketones, and that far less energy is required to bring about the gelation of rubber sols than the liberation of methyl groups from acetone.

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# THE COURSE OF AUTOÖXIDATION REACTIONS IN POLYISOPRENES AND ALLIED COMPOUNDS.

## PART. VI. THE PEROXIDATION OF RUBBER\*

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Peroxides have repeatedly been shown to appear during the slow oxidation (perishing) of rubber in air, and during both its milling in air and the passage of air or oxygen through its solutions: yet in none of the recorded experiments has the production of any very substantial proportion of peroxide been demonstrated. This arises largely because, under many conditions of autooxidation, no very considerable proportion of peroxide is present in the oxidation product at any stage, but in part because no convenient and reasonably accurate method of determining the peroxide content in so insoluble a substance as rubber has been available. It must inevitably happen in a long-chain molecule of polymer-homologous type containing on the average about 5,000 autoxidisable olefinic units that the progressive entrance of a heterogeneous element will yield a large variety of closely similar products if attack is fairly evenly distributed over the chain, but when, as in the case of oxygen, the heterogeneous element enters the hydrocarbon as a diatomic molecule, the atoms in which can ultimately separate and become attached to the carbon chain in a variety of ways, and causes, as the result of its progressive incorporation, scission of the chain at an ever-increasing number of the olefinic units, then the potential range of diversity of the products becomes enormously increased.

*General Course of Autooxidation Reactions.*—In consequence of the above-mentioned diversity, it is perhaps not surprising that examination of the character of many scores of (catalyzed) thermal oxidation products obtained by one of us with E. S. Narracott over a fairly wide range of oxygen input has given little detailed information respecting the course of autooxidation (details are omitted from the present communication). These products were, in general, neutral, *i.e.*, insoluble in aqueous alkali, up to the oxidative stage at which about 0.9 atom of oxygen per isoprene unit had been supplied to the hydrocarbon, and after this stage increasingly acidic until, at the highest stage of oxidation attained, *i.e.*, at 30 per cent of oxygen input and temperature above 70°, only acidic materials were obtained. The average molecular weight of the oxidation products decreased rapidly as oxidation proceeded, that of the neutral products being reduced ultimately to a few thousand units<sup>1</sup> and that of the acidic products, judged by their equivalent weights<sup>2</sup>, ultimately to about 700–800 units. It thus appears likely that the oxidative scission reactions which are responsible for the reductions in molecular weight produce in the first place fragments with neutral end groups (presumably —CHO and —CO·CH<sub>3</sub>, through severance of the polyisoprene chains at the double bonds), and these end groups in the main escape further oxidative attack (to give

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carboxyl groups) until a fairly definite overall stage of oxygenation is reached. Oxidative degradation of the rubber, however, was not confined to the production of shortened and somewhat oxygenated chains: there were always formed, even from the outset of reaction, small, but not negligible, proportions of water and carbon dioxide—and possibly also traces of other volatile compounds such as the carbon monoxide and hydrogen observed by Dupont<sup>3</sup> to accompany water and carbon dioxide in the autooxidation of cyclohexene and methylcyclohexene—and these volatile substances must, from the constancy of their formation from purified as well as from impure rubbers, be regarded as secondary decomposition products of the rubber itself, and not merely of the nonhydrocarbon components in the rubber.

Recent experiments have shown that the primary autooxidation products of rubber and of other olefins, *i.e.*, peroxido derivatives, survive in better yield under photochemical conditions of formation than under thermal conditions, provided exposure to light is not too prolonged; hence the photochemical products lend themselves more readily to investigation of the first stage of autooxidative reaction than do the corresponding thermal products. Preliminary runs under photochemical conditions, a petroleum-soluble fraction of rubber dissolved in benzene being used, have given liquid or resinous products generally comparable as regards their neutral or acidic character and their degraded condition with the above-mentioned products of thermal oxidation, but showing considerably higher peroxide yields in the earlier stages of reaction. The details in Table I refer to representative products obtained at about 35° over

TABLE I

PHOTOÖXIDATION OF PETROLEUM-SOLUBLE RUBBER (IN BENZENE) AT ABOUT 35°.

Approximate oxygen input (percentage)*	Character of product	Oxygen content (percentage)	Atoms per C <sub>6</sub> H <sub>8</sub>	Peroxidic oxygen (%)	Iodine value		M
					Found	Calc.†	
2	Neutral, ether-soluble	2.0	0.09	1.3	356	348.6	80,000
7	" "	6.95	0.32	2.7	312	290	—
8(a)	" " (94%)	7.9	0.37	1.2	308	280	—
(b)	ether-insoluble (6%)‡	9.4	0.44	—	—	—	—
13	" ether-soluble	11.6	0.56	4.0	265	238	—
(a)	" " (3%)	18.1	0.94	5.4	220	162	2,100
22(b)	Acidic, " "	20.55	1.10	0.0	—	—	—
(c)	ether-insoluble (3%)	27.15	1.58	0.0	—	—	—
(a)	" ether-soluble (33%)‡	18.7	0.98	0.1	214	155	—
32(b)	" " (15%)	30.2	1.84	—	—	—	—
(c)	ether-insoluble (52%)§	27.5	1.69	0.0	115	40.7	1,300

\* Based on weight of rubber taken.

† Insoluble in all the ordinary solvents for rubber.

‡ This portion separated out in the form of its sodium salt on shaking the ethereal solution of the oxidation product with alkali.

§ Soluble in alcohol.

¶ Calculated on the ring-peroxide hypothesis<sup>4</sup>.

a range of oxygen intake from 2 to 25 per cent, the intake being determined approximately from the change in gas volume, and the oxygen content of the product more exactly by careful ultimate analysis.

In all these preliminary runs, the iodine values of both neutral and acidic products were higher than would have obtained if the ingoing oxygen had added at, and had so saturated, an equivalent proportion of the olefinic double bonds in the rubber molecule. Both the neutral and the acidic products contained a high proportion of hydroxylic oxygen, determined by the Zerewitinoff method, which amounted in the early stages of oxidation to rather more than half the total oxygen content,<sup>5</sup> but fell off somewhat later. Products of neutral character survived down to a molecular weight of about 2000. In all cases, the



acidic products contained more oxygen than the corresponding neutral products, but none of the acidic substances contained more than a trace of peroxidic oxygen, although it is to be borne in mind that the use of solutions of caustic alkali in separating acidic from neutral products inevitably causes some peroxidic decomposition, with concomitant oxidative attack elsewhere in the system.<sup>6</sup>

*Early Stages of Autooxidation.*—The net result of the foregoing photooxidations was to produce a series of oxygenated rubbers in which at best only about 65 per cent of the ingoing oxygen survived at the end of the operation in peroxidic form. Since, under the most favorable conditions of oxidation discovered, the ratio of peroxidic oxygen surviving in the product to ingoing oxygen declined rapidly with increasing oxygen intake (pointing to the inevitable onset of secondary decay reactions), it was necessary, in investigating the structural character of the undeteriorated peroxido derivatives, to work with lightly oxidized rubbers. Even so, success in arriving at definite conclusions was governed wholly by ability to measure with reasonable accuracy: (1) the oxygen intake of the rubber, and (2) the peroxidic oxygen content of the products together with their active hydrogen value and unsaturation. The most troublesome of these measurements was that of the oxygen intake, which had to be made under fluctuating temperature conditions in the presence of a volatile hydrocarbon solvent, some water vapor, and traces of carbon dioxide; the principal error, due to the solvent vapor, could be eliminated by use of a compensating device, but the residual error was still  $\pm 5\%$  as a maximum. For the determination of active hydrogen values (and hence of the corresponding hydroxylic oxygen values) the method of Bolland, devised for the purpose, has given very satisfactory and consistent results. With respect to the determination of unsaturation in rubbers, no method hitherto described approaches in accuracy and consistency that of the iodine value method<sup>7</sup> under conditions of operation essentially as described by Kemp<sup>8</sup>, and it has proved easily possible by careful attention to experimental procedure to duplicate results consistently within 1 unit, i.e., to reduce the error of observation in the present experiments to within  $\pm 0.3$  per cent.

In tracing the changes in oxygen content, peroxide content, active hydrogen value, unsaturation, and molecular weight from stage to stage during the earlier course of oxidation, it proved impracticable either to carry out carefully controlled oxidation on a large enough scale to supply representative samples for all of the numerous observations required at each of the oxidative stages, or even to secure sufficiently accurate measurement of the oxygen intake when absorption was interrupted at the end of each stage for the removal of test samples. It was found best to carry out a separate oxidation (from the same batch of rubber solution) for each oxidative stage, while keeping the intensity of illumination and the temperature as constant as possible through all stages. This procedure had the disadvantage that the curves representing variation of the individual functional values over the whole course of oxidation covered were somewhat less smooth than would otherwise have been the case (since small differences in illumination, reaction temperature, etc., from experiment to experiment were impossible to avoid), yet in all essential respects it proved satisfactory.

*Peroxide Yield.*—Determination of the variation of peroxidic oxygen content from stage to stage over the earlier course of photooxidation of rubber has, because of its importance, been carried out both in a series of separate single-stage experiments spread over the range of oxygenation to be covered,



and in a single multi-stage experiment with interruptions at different oxidative stages. Curve II (Figure 1) shows the respective results in relation to the oxygen intake, the circles representing the results of the single-stage experiments and the squares those of the multi-stage experiment. The yield of peroxide falls off steadily from 80 per cent at just less than 0.05 atom to 38 per cent at 0.41 atom of oxygen per  $C_5H_8$  unit. The highest peroxide yields yet measured by us in these early stages fall around 90 per cent of the oxygen intake, and if our methods of experimental determination were sufficiently exact to be applicable in the still earlier stages, they would probably show a value approaching 100 per cent. It may well be, although it is not proved, that at all stages in the photoöxidation of rubber the whole of the ingoing oxygen is incorporated in the first place in peroxidic form.

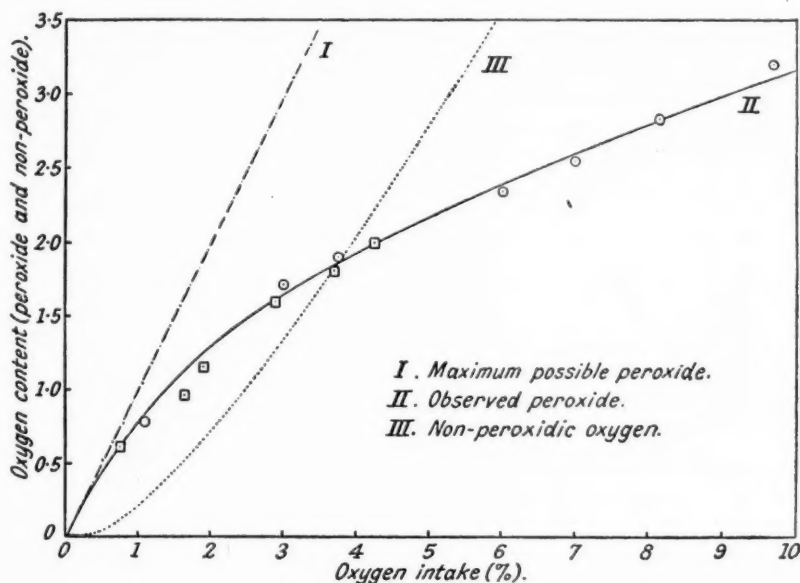


FIG. 1

**Character of the Peroxide Groups.**—It has been noted above that increase in the oxygen content of oxidized rubbers is consistently accompanied by increase in the active hydrogen content. Since existing evidence indicates that the normal decomposition product of a hydroperoxide formed in the absence of special decomposition catalysts is the corresponding alcohol (the active oxygen atom of each hydroperoxide group being expended in oxidative attack at a near or remote double bond), it is to be expected that each molecule of oxygen absorbed will inevitably produce one hydroxyl group (this either forming part of an original  $\cdot OOH$  group or appearing as a secondarily formed  $\cdot OH$  group), and this expectation will hold, provided that all the peroxide groups formed in rubber are hydroperoxide groups and that no secondary condensation or dehydration reactions occur in the oxidized rubber. Therefore, in the absence of the latter types of secondary reaction, and complete initial incorporation of the oxygen in the form of  $\cdot OOH$  groups being assumed, the

observed hydroxylic oxygen content of any oxidation product is likely to be half the value of the corresponding oxygen intake. The hydroxylic oxygen content can be determined with reasonable precision *via* the active hydrogen content, and the degree of departure of the experimental from the calculated hydroxylic oxygen values is shown in Figure 2 (curves I and II). It is seen that, in the very early stages of oxidation, where nearly all of the oxygen present occurs in peroxide groups, there is little deviation of the observed from the calculated values and, hence, the peroxide groups themselves cannot be other than hydroxylic (*i.e.*, hydroperoxidic). Later, however, when peroxide decay is rapid and the proportion of secondarily-formed hydroxyl groups should, in terms of the hypothesis, have become important and be increasing steadily, the observed hydroxylic oxygen values are seen to fall short of the calculated ones, *e.g.*, by 15 per cent at 4.25 per cent oxygen intake. The falling off must be attributed either to disappearance or to non-formation of the simple hydroxyl groups.

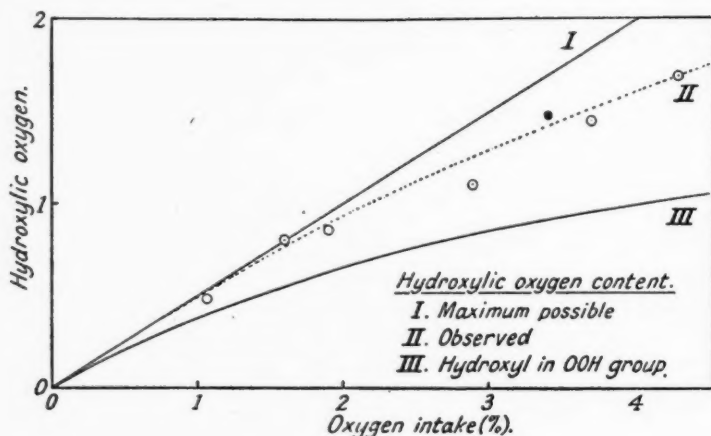


FIG. 2

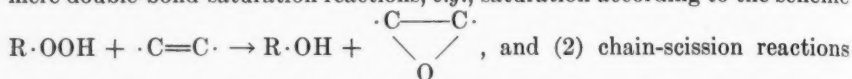
The steady overall increase in the proportion of simple hydroxyl groups as oxidation proceeds is to be seen in Figure 2 by subtracting the ordinates of curve III (expressing the change in the hydroxylic oxygen content of the hydroperoxide groups, *i.e.*, in the half-values of the observed peroxidic oxygen contents shown in curve II, Figure 1) from the ordinates of the curve II, Figure 2 (expressing the change in the observed total hydroxylic oxygen). There is nothing to indicate that the progressive falling away from the expected hydroxylic values is due to the formation of something less than one hydroxyl group per peroxide group, *e.g.*, as the result of some degree of ketone formation in place of alcohol formation<sup>9</sup>. On the other hand, there is abundant evidence that oxidized rubbers lose water readily and unavoidably on keeping, and more readily still on heating; and indeed, the tendency represents an ever-present complication in the compilation of accurate quantitative data concerning the oxidation of rubber, owing to the impossibility of drying specimens to constant weight at temperatures above room temperature. In the present experiments, consistent results have been obtained by drying the samples in a high vacuum

at room temperature and making determinations on them as far as possible within two days of their isolation from the solvent: the result of mere keeping of the specimens for a week in a high vacuum at room temperature is seen in the rather low hydroxylic oxygen values at two points on curve I, Figure 2. The gradual loss of water promoted by warming the oxidation products at reduced pressures leads to increased viscosity of solutions of the products and to increased molecular weight, and on this account it seems likely, although it is not formally established, that the elimination of water results in ether formation (largely intermolecular) rather than in the production of double bonds by dehydration. The existence of this secondary tendency to the spontaneous loss of water<sup>10</sup> being taken into account, the production of hydroxyl groups is in fairly satisfactory agreement with expectation on the basis of the hydroperoxidation hypothesis.

*Effect of Peroxidation on the Unsaturation.*—Peroxide groups formed by the action of oxygen on olefins can be hydroperoxidic only if they are formed by introduction of the reagent at one or other of the methylene groups of the chain, so leaving the olefinic unsaturation intact. Hence in the very early stages of the oxidation of rubber the original unsaturation of the rubber should be undiminished, although as peroxide decay gets under way saturation of the double bonds will take place increasingly, as it does in the olefinic systems already considered. To demonstrate the uniform occurrence of hydroperoxidation throughout the process of oxygen absorption, it must be shown that the degree of unsaturation surviving at any stage in the reaction is quantitatively related to the fraction of the absorbed oxygen which remains at that stage in peroxidic form. Such a demonstration, however, can be successful only in the comparatively early stages of reaction where to no serious extent is peroxidizing power being consumed in post-saturation processes, *i.e.*, in chain-scission reactions requiring the expenditure of active oxygen beyond the stage at which one such active atom (from one  $\cdot\text{OOH}$  group) has been used in saturating one double bond.

The experimental results obtained for lightly oxidized rubber are shown in Figure 3, where: (1) curve I represents the small change in overall unsaturation (expressed by decrease in the iodine value) which would obtain if all the oxygen entered in hydroperoxidic form and no peroxide-decay occurred; (2) curve II represents the rapid diminution of unsaturation which would occur if the ingoing oxygen molecule added at, and saturated the double bonds, and (3) curve III connects a series of pairs of points (circles and triangles), each pair referring to one of a series of separate experiments spaced over the early stages of oxidation, *i.e.*, up to a 5 per cent oxygen intake, and one point in each pair representing the experimentally observed diminution of unsaturation and the other the corresponding calculated value derived, as indicated above<sup>11</sup>, from the proportions of peroxidic and nonperoxidic oxygen found in the rubber at the different points of observation. The agreement between the observed and calculated values is very good in view of the known error in the methods of determination. The disappearance of unsaturation as oxidation progresses is substantial, amounting even as early as 2.6 per cent of oxygen intake to nearly 50 per cent of that possible on the double-bond-addition hypothesis; the rate of disappearance of unsaturation, however, appears to settle down to a roughly steady rate ( $>$  half the maximum calculated on this hypothesis), although since each pair of points on curve III represents a separate oxidation, with unavoidable slight differences in conditions from experiment to experiment, the true slope of the curve may differ slightly from that shown.

*Chain-scission Reactions.*—The distribution of the active oxygen which is rendered available for oxidative purposes during peroxide decay between (1) mere double-bond-saturation reactions, *e.g.*, saturation according to the scheme



has not yet been closely studied. Certain observations of interest, however, have been made. In Figure 3, curve IV, is shown the progressive diminution

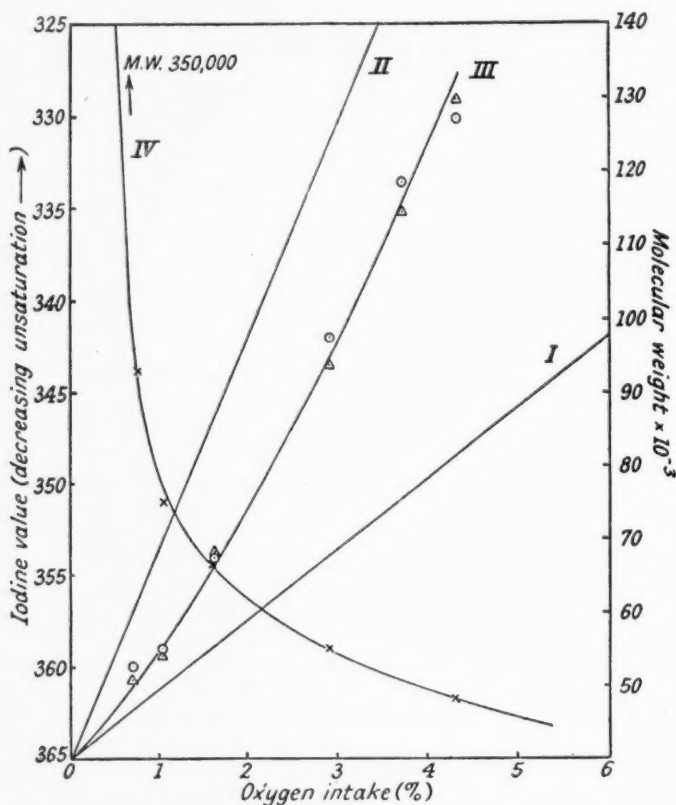


FIG. 3

in molecular weight of the rubber samples used above over a course of oxidation ranging from 0 to 4.3 per cent of oxygen intake. The most spectacular diminution comes, of course, in the very early stages of oxidation, where, apparently, minute proportions of oxygen can have a profound effect; *e.g.*, an intake of about 1 per cent of oxygen is sufficient to reduce the molecular weight from 350,000 to about 75,000. The stoichiometric features of this degradation, however, deserve some scrutiny. From the decrease in molecular weight, the number of double bonds broken can be determined, and from this number together with the corresponding oxygen intake value, the average number of

oxygen atoms which are absorbed by the rubber in severing one C—C bond can be calculated. This number is seen from Table II to be considerable, and to rise as oxidation progresses. It would seem, therefore, that no very simple scheme for the utilization of oxygen for scission purposes, *e.g.*, such a scheme as Staudinger's, expressed by  $\cdot\text{C}=\text{C}\cdot + \text{O}_2 \rightarrow \cdot\text{CO} + \cdot\text{CO}$  is likely to be correct unless there exists a special capacity on the part of some few of the incorporated oxygen molecules, *e.g.*, in  $\text{R}\cdot\text{OO}\text{—}$ , for effecting scission.

Two points, however, with regard to this number of oxygen atoms absorbed per double bond broken are to be borne in mind. First, it represents only a very rough estimate since, to take reasonably accurate account of the oxygen which is consumed in producing (concomitantly with the scission) the small amounts of water and carbon dioxide which are known to be formed, it would be necessary to determine the oxygen intake correctly within  $\pm 0.01$  per cent—a requirement quite unattainable with solutions of rubber. Secondly, the number comprises not only those of the original oxygen molecules which expend their oxidizing power (more or less directly) in effecting the scission of a C—C bond, but all those other oxygen molecules which are concurrently incorporated

TABLE II  
DEGRADATION OF RUBBER DURING OXIDATION (IN CYCLOHEXANE).

Oxygen intake, %	Mol. wt. of product (in benzene)	Oxygen atoms per mol. introduced	Number of bonds broken	Oxygen atoms absorbed per bond broken
0.00	324,000	—	—	—
0.75	93,000	152	2.50	60.8
1.04	75,000	210	3.32	63.5
1.62	67,000	343	3.83	87.6
2.9	55,000	587	4.90	120.0
4.3	48,000*	871	5.75	151.1

\* In benzene + methyl alcohol.

in the rubber chain (as  $\cdot\text{OOH}$  groups or their decay products) without actually causing scission. No close estimate, therefore, can be made of the average oxygen expenditure in purely scission reactions.

Bound up with the question of oxygen utilization in chain-scission processes is the problem of scission mechanism. It is conceivable that peroxidic radicals  $\text{R}\cdot\text{OO}\text{—}$  play some small part in the attack on double bonds, but for the most part the scission mechanism seems to depend on the oxidative action of completely-formed hydroperoxide molecules,  $\text{R}\cdot\text{OOH}$ . Whether epoxy-compounds represent usual intermediates in the scission process remains to be determined, but the subject of chain-scission mechanism can be studied more suitably with comparatively small olefinic molecules than with rubber, and is left for future investigation.

**Conclusions.**—(1) High yields of peroxides (80–90 per cent) are to be observed in the early stages of the photooxidation of rubber, but later on, decay reactions occur to a serious degree. Both the primary and the secondary products of oxidation are hydroxylated.

(2) The observed unsaturation and active-hydrogen values of the peroxidized rubber formed in the early stages of oxygen absorption are incompatible with the view that oxygen adds at the double bonds of the rubber; on the contrary, they are quite compatible with the view that incorporation of the oxygen results in the formation of hydroperoxide groups.

(3) Oxidative scission of the chain-molecules begins at the outset of oxida-



tion and rapidly reduces the molecular weight. The quantity of oxygen absorbed by the rubber at any point in the oxidation appears to be more than adequate, stoichiometrically, to bring about scission of the chains by multi-stage mechanisms at the required number of unsaturated centres to correspond with the observed reduction in molecular weight. The precise mechanisms involved, however, are obscure, and may involve in some small measure the reaction of radical intermediates such as  $R\cdot OO-$ .

(4) Water and carbon dioxide are formed in small proportions from the earliest stages of autoxidation, and elimination of water continues after the oxidation products have been isolated.

### SUMMARY

#### EXPERIMENTAL

*Materials.*—(1) *Rubber.* For convenience, a sol fraction of rubber, obtained by partial dissolution of crepe rubber in light petroleum (b.p. 40–60°), was employed. The crepe rubber was cut up and thoroughly extracted with acetone in the usual manner, and the residue then extracted with light petroleum in the all-glass modification of Pummerer, Andriessen, and Gündel's apparatus described by Bloomfield and Farmer<sup>12</sup>. In the latter operation, the extracts obtained in the first 48 hours were rejected as containing oxygenated rubber, and the later extracts were well mixed and their rubber content precipitated by addition of excess of 95% alcohol. In the earlier experiments, the solvent and alcohol adhering to the rubber were removed by evaporation at 15 mm. pressure, and the rubber was finally dried at 0.5 mm. and 56° in a pistol drier. The dried rubber was stored in purified nitrogen in a desiccator, the nitrogen being removed by evacuation and replaced every 48 hours. For the later experiments the precipitated rubber was freed from solvent and alcohol by evaporation first at 15 mm. and 30°, and then at 0.5 mm. and room temperature, and finally it was dried for 48 hours at 10<sup>-5</sup> mm. and room temperature. The rubber so obtained was rapidly cut up into small pieces (2 mm. thick), placed in glass tubes in 2-g. or 5-g. batches, and the tubes evacuated on a high-vacuum line for 4–6 hours and then sealed carefully while still attached to this line. The tubes were covered with black paper and kept in the dark until required. Samples of "sol" rubber so stored retained over long periods their physical and chemical properties without any detectable deterioration. The following values are typical of samples prepared in this way: N, 0.09; ash, 0.065; C, 87.65; H, 11.85; P.O.C., <0.02%; *M*, 324,000.

(2) *Nitrogen.* In all operations with rubber, its solutions and derivatives in which desired oxidation was not in progress, or vacuum conditions obtaining, the containing vessel was filled with purified nitrogen, commercial "purified nitrogen", which had been freed from residual oxygen by Fieser's process, being used.

(3) *Chloroform.* The "AnalaR" reagent gave consistent results when used as solvent for iodine-value determination.

(4) *Carbon disulfide.* The colorless "AnalaR" reagent was quite satisfactory for iodine-value determinations, but when through long storage after it had been exposed to air the reagent became yellow, it was distilled over and stored over sticks of sodium hydroxide.

(5) *Cyclohexane.* The commercial hydrocarbon was shaken for 24 hours with a 20% oleum (changed after 12 hours), very thoroughly washed with alkali and with water, and finally rectified under a jacketed Widmer column.



*Preliminary Experiments*

*Method of oxidation.*—A 2% solution of rubber in purified benzene was placed in a 500-cc. quartz flask fitted with a mechanical stirrer (mercury seal) and with a side arm. The side arm was connected through a calcium chloride tube to an oxygen reservoir, and the air in the flask was displaced by oxygen. The flask was illuminated and somewhat warmed (about 35°) by a Hanovia mercury-vapor lamp, S. 500, placed 6–8 inches away. After a short induction period (<1 hour), the stirred solution began to absorb oxygen, and absorption proceeded fairly rapidly. The gas volume absorbed was read directly, and corrected only for temperature and pressure. For the lower stages of oxidation 250-cc. portions of 2% rubber solution were taken, and for the higher stages 500–1000-cc. portions. The duration of oxidation varied from 2 to 80 hours.

*The oxidation products.*—The reaction mixture was freed from solvent by distillation under reduced pressure, and, in the case of those products containing less than 10% of oxygen, the residue was divided into ether-soluble and -insoluble fractions by agitation with peroxide-free ether. At the more advanced stages of oxidation, it was necessary to redivide the ether-soluble fraction into neutral and acidic portions by shaking the ethereal solution with dilute aqueous sodium hydroxide (or sodium bicarbonate). The separation of the aqueous alkaline layer from the ether layer was usually very slow, owing to emulsification, and hence there was some unavoidable diminution in the (already small) peroxide content of the separated materials due to the action of alkali, and doubtless in consequence a corresponding small increase in the degradation of the oxidized rubber. On each of the products determinations for carbon, hydrogen, oxygen (diff.), P.O.C., and iodine value were made, and in the case of certain of the products determinations for hydroxylic oxygen (Zerewitinoff) and molecular weight (viscosity). The essential data are listed in Table I.

*Later Experiments*

*General procedure.*—Owing to practical difficulties in uniform cooling and effective irradiation of a large vessel during shaking, and to serious inaccuracies arising from (1) frequent interruptions of the oxidation process, (2) the difficulty in withdrawing at each stage numerous carefully measured portions of the viscous solution without incurring any loss, and (3) severe depletion of the stock (tending to make the samples unrepresentative) towards the end of the process, the multi-stage procedure was used only for checking the trend of variation in the proportions of single functional groups, and particularly for observing the relation of peroxide formation to oxygen absorption, since this required the withdrawal of only 2–3 cc. of solution at each oxidative stage. For the purpose of following the structural changes occurring in the early stages of oxidation, a series of separate oxidations spaced over the range of oxidation to be studied was found advantageous. The adoption of this procedure made it necessary to maintain the temperature and illumination as constant as possible during all stages of the oxidation, and to employ a standard method of withdrawal of samples and isolation of the oxidized rubbers. All oxidations were conducted in carefully purified cyclohexane at 12°, with fairly rapid shaking, the ultraviolet lamp being placed 4 inches from the oxidation vessel.

*The oxidation vessel* (Figure 4).—This consisted of a 300-cc. Pyrex flask, *A*, connected with a manometer and compensator, *B*. The compensator, which

was connected to one side of the manometer with a cone and socket joint (B 10 size) secured with spring clips, contained 1–2 cc. of the pure solvent, and served to compensate (when tap *C* was closed) for the partial pressure of the solvent in the reaction vessel. The compensator was easily detachable for cleaning purposes. The volume of the vessel was 343 cc.

The free space in the vessel was the difference between the volume of the apparatus and the volume of the rubber solution ordinarily taken, *i.e.*, 343–100 cc. To this had to be added the volume of gas dissolved in the solvent, *viz.*, 0.15 cc. per cc. of cyclohexane. Hence the total effective gas space was  $[243 + (100 \times 0.15)]$  cc. = 258 cc.

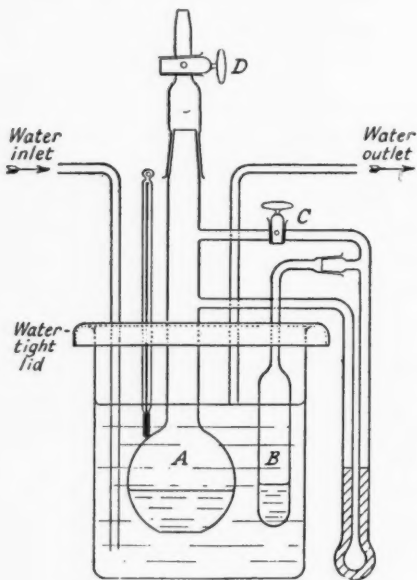


FIG. 4

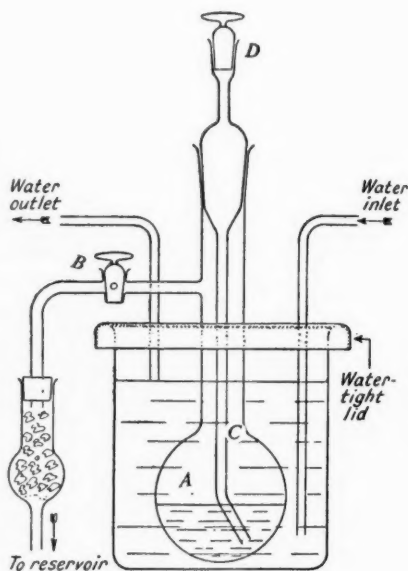


FIG. 5

At the start of each experiment the mercury stood at the same height in the two arms of the manometer. When tap *C* was closed and the oxidation began, the pressure in flask *A* diminished owing to consumption of oxygen, and this caused a shift of the mercury level towards *A*. The gas space in *B* thus became greater and that in *A* slightly smaller, but whereas the change in volume in *A* was negligible compared with the total gas volume (258 cc.), that in *B* was significant, and could not be neglected in determining the true change in oxygen pressure. To permit measurement of the latter, the manometer had already been calibrated against a standard manometer before introduction of solution and solvent into *A* and *B* respectively. The true change of pressure in *A* was found to approximate closely to the observed change in pressure  $\times 1.075$ , for the range of change of pressure observed.

For measurements where the oxygen intake to be employed was in the range 0.5–2.0%, a charge in the flask of 2 g. of rubber in 150 cc. of cyclohexane was advisable; where the intake was to exceed 2% a charge of 1 g. of rubber in 100 cc. of solvent was sufficient. With these quantities, the accuracy of

measurement of the oxygen intake fell within  $\pm 5\%$  of the true value. The charge was prepared by shaking mechanically (12 hours) a weighed sample of sol rubber (see above) together with the requisite amount of cyclohexane in a 150-cc. bottle from which all air had been removed by evacuation and its place taken by purified nitrogen. The rubber solution was transferred to the oxidation apparatus by means of a funnel having a long stem, and the funnel and bottle were well washed with a further 50 cc. of solvent. Then the compensator was charged with 1-2 cc. of pure solvent and reattached to the manometer arm.

The whole reaction vessel was cooled in ice water until the cyclohexane had completely frozen; then it was evacuated with an oil pump (using an interposed liquid-air trap) with taps *C* and *D* open; finally, oxygen was admitted, up to 400 mm. pressure. Tap *D* was then closed, and the vessel enclosed in a beaker provided with close-fitting lid, water inlet and exit tubes for water-cooling, and a thermometer. The apparatus was mounted on a shaker near to a Hanovia mercury vapor lamp, S 500. The apparatus was shaken, water at  $12^\circ$  was circulated through the beaker for 30-60 min. (tap *C* open) to permit equilibrium to be established throughout the system; then tap *C* was closed and the lamp switched on. After the desired stage of oxidation had been reached, the lamp was switched off and the apparatus shaken for a period to allow equilibrium to be established again. The difference in height of the mercury columns in the two arms of the manometer was read. The temperature of the cooling water was maintained constant throughout. The percentage weight of oxygen absorbed was given by  $32(p/760)(V/22,400)(100/W)(273/T)$ , where *p* is the corrected change in pressure, *V* the total gas space, *W* the weight of rubber in solution, and *T* the absolute temperature.

*Measurement of oxygen intake.*—In the early stages of reaction the method described above is employed; in the later stages the observed intake (%) can be checked by calculating the oxygen absorbed (%) from the oxygen contents of the product and of the original rubber, each of these being determined (by difference) from careful carbon and hydrogen determinations. No generally effective way of compensating for the small amounts of water, carbon dioxide, or other highly volatile materials formed during the oxidation has been found, and hence the error due to this cause is left uncorrected.

*Determination of peroxidic oxygen.*—The method already described by Bolland *et al.* (*Trans. Inst. Rubber Ind.*, 1941, 17, 29) was used. For lightly oxidized rubbers there is great danger of partial precipitation and consequently incomplete reaction when the reagent is added to their solutions; hence, when the total oxygen content is below 15%, the recommended mixture (73 : 27, by vol.) of benzene and methanol for dissolving the ferrous thiocyanate reagent must be strictly employed. When, however, the oxygen content of the oxidation product exceeds 15%, admixture of benzene with the methanol can be dispensed with.

*Determination of active hydrogen.*—This proceeded satisfactorily by the method of Bolland (*ibid.*, 1941, 16, 267) when the solvent employed for the oxidized rubbers was dry toluene and the Grignard reagent was made up first in dry ether and the uncombined ether subsequently removed completely in a high vacuum and replaced by dry xylene.

*Determination of unsaturation.*—As with other polyisoprenes studied, the most consistent and precise values for the unsaturation of rubber have been obtained by the iodine-value method. Halogens possess considerable powers of substitution when reacting with olefinic substances, including rubber. The

conditions under which iodine chloride reacts quantitatively and conveniently with rubber have been closely investigated by Kemp (*loc. cit.*) and Kemp and Mueller (*loc. cit.*); we have found the latter's method to be very satisfactory over a wide range of conditions, but we had slightly to modify the procedure developed for rubber to render it applicable to oxidized rubbers.

Kemp and Mueller<sup>2</sup> used carbon disulfide as solvent for rubber, but, for oxidized rubbers, chloroform is a more satisfactory solvent<sup>15</sup>. We found 50 cc. of chloroform to suffice to dissolve *and retain in solution* oxidized rubbers containing >5% of oxygen, but 75 cc. are required for products containing <5% of oxygen. Great care is necessary in the addition of Wijs's solution to avoid precipitation of rubber; it should be slowly and cautiously released from a pipette, with calcium chloride tube attached<sup>17</sup>, on to the sides of the bottle, and if a wide-mouthed bottle is used for the determination, there is no difficulty in doing this while at the same time imparting a rotatory motion to the rubber solution. In this way an undue concentration of the added reagent at one point is avoided. If precipitation of the rubber accidentally occurs during addition of the reagent the determination is abandoned; later, when the reagent has fully reacted with the rubber, precipitation does not matter.

The operation is then conducted in the way described by Kemp and Mueller, as except as regards one detail. Previous work on the autooxidation of cyclohexene<sup>16</sup> showed that even the slightly peroxidized hydrocarbon gives too low iodine values, owing to reaction of the peroxide with excess of the potassium iodide used in the determination. In the case of oxidized rubbers, the effect of peroxide groups is much less but is not negligible. It is found that the undesired reaction can be greatly suppressed by using 100–150 cc. of water for dilution purposes instead of the 75 cc. recommended by Kemp. This serves substantially to eliminate error due to peroxidic action.

The end-point with most samples can be obtained within half a drop of thiosulfate, if the latter is well washed down and thoroughly incorporated in the test solution by vigorous shaking. The accuracy of determination is thus within  $\pm 0.3\%$ .

**Multi-stage oxidations.**—The rate of formation of peroxidic groups with increasing oxygen intake was conveniently followed in a multi-stage experiment using the apparatus illustrated in Figure 5. This consisted of a liter flask *A* as receptacle for the rubber solution, to which was attached a side arm (carrying a tap *B* and calcium chloride tube) for making connexion with the oxygen reservoir. The neck of the flask was closed by a ground-in hollow stopper, the lower end of which was sealed to a glass tube *C*, bent as shown, reaching nearly to the bottom of the flask, and the upper end to a short tube fitted with a ground-in stopper *D*. The tube *C* was required for the withdrawal of samples.

Ten g. of sol rubber of low peroxide content were dissolved in 400 cc. of pure cyclohexane contained in a stoppered bottle (nitrogen atmosphere), a mechanical shaker being used. The solution was transferred to the flask *A*, the bottle being rinsed out with a further 100 cc. of cyclohexane. The tube *C* and stopper *D* were placed in position, and the flask evacuated by means of an oil-pump (tap *B* open). In this operation, the flask was tilted so that the lower end of *C* cleared the surface of the liquid in the flask. Tap *B* was then closed, the flask was enclosed in a covered beaker, acting as cooling jacket, through which cold water at constant temperature (14°) circulated, and the whole was mounted on a mechanical shaker. The flask was connected to the oxygen reservoir, and filled with oxygen; then, after a short period of gentle shaking, the gas in both was brought to atmospheric pressure. The volume

of gas in the reservoir and its temperature were noted. Then a mercury vapor lamp placed 4 inches from the flask was turned on, and the flask shaken rapidly.

At the end of each oxidative stage the lamp was turned off, the flask was shaken slowly for 30–45 min. to ensure that equilibrium had been reached, and the volume of gas remaining in the oxygen reservoir (after adjustment of the pressure to atmospheric pressure) and the temperature were observed. The stopper *D* was then removed, the level of solution in the tube *B* was raised by increasing the pressure in the oxygen reservoir, and a sample (exactly 3 cc.) of the reaction product removed for peroxide determination by means of a long-stemmed graduated pipette. Since any unmeasured loss of solution would entail inaccuracy in the later stages of oxidation, it was necessary to avoid undue wetting of the walls of the pipette. The results of a typical multi-stage oxidation are shown graphically in curve II, Figure 1 (dots in circles).

*Single-stage oxidations.*—These were conducted at about 12° in the apparatus described above (Figure 4). As soon as the oxidation of a sample was complete, the oxidized solution was pipetted into a cylindrical evaporation vessel, 55 mm. wide, fitted with interchangeable, flange-jointed lids suitable for attachment to a vacuum line or for use in distillation of the solvent. 10–15 cc. portions of the solution were immediately taken for determination of the peroxidic oxygen content and the active hydrogen content of the oxidized rubber; an aliquot portion was also taken for determination of the concentration of oxidized rubber therein. Since all the necessary determinations could not be made at once (the determination of active hydrogen alone took 6–8 hours) the remainder of the solution was treated as follows. The solution was freed from solvent by evaporation at 15 mm. pressure and 30°, and the residue then dried completely in the flange-jointed vessel at room temperature—first at 0.5 mm. for 2–4 hours, and finally at  $10^{-5}$  mm. for 24–30 hours. The oxidized rubber at the end of this drying process was entirely free from solvent. The dry, oxidized material was kept attached to the vacuum line at room temperature until all the analytical determinations (iodine, peroxide, and active hydrogen values, and molecular weight) had been satisfactorily completed; when, however, samples were to be withdrawn the flange-jointed vessel was filled with dry nitrogen before being removed from the vacuum line. When the required sample had been quickly removed, the flange-jointed vessel was returned to the vacuum line and re-evacuated. All samples withdrawn for analytical measurements were protected against bright sunlight and were weighed and used promptly. Peroxidic oxygen determinations were usually made with measured volumes of the solution immediately after the oxidation was completed and again with a dried sample: the difference between the values so obtained was small. All samples of oxidized rubber lost water very slowly in a high vacuum even at room temperature, and this loss increased considerably as the temperature rose. For this reason, samples which had been kept at room temperature for 7 days gave unduly low values for the active hydrogen content—a contingency which was not at first realized.

All molecular-weight determinations were made by the viscosity method. The following details apply to a typical run: 1.5 g. of sol rubber (iodine value 365.0) in 150 cc. of cyclohexane were oxidized at 11° for 90 min. The change in pressure corresponding to a free space in the vessel of 208.0 cc. was 29.0 mm. The oxidized material gave the values: oxygen intake, 0.75; P.O.C., (in solution) 0.62, (dry) 0.60%; iodine value, 360.0, 359.4, 360.0 [calcium: (1) on basis of saturation effected by the nonperoxidic oxygen, 360.8; (2) on basis of ring



peroxide hypothesis, 356.0];  $M$ , 93,000. The progressive change in the respective values from stage to stage in the oxidation is shown graphically in Figures 1-3.

#### ACKNOWLEDGMENT

We thank G. Gee for carrying out the molecular-weight determinations. The work described in this and the two preceding papers has been carried out as part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

#### REFERENCES

- <sup>1</sup> The (viscosity) molecular weights in this paper are calculated by the use of Gee's constant for rubber. The average molecular weight of unoxidized rubber on this basis is 350,000, *i.e.*, about 2.5 times that which would be obtained by using the formerly accepted constant of Staudinger.
- <sup>2</sup> The acids are assumed to be monobasic.
- <sup>3</sup> Dupont, *Bull. soc. chim. Belg.* **45**, 57 (1936); **46**, 21 (1936).
- <sup>4</sup> *J. Chem. Soc.* **1942**, 122.
- <sup>5</sup> For the accurate measurement of small concentrations of hydroxyl in high-molecular compounds, the Zerewitinoff method is unsuitable, and has been superseded in our later determinations. Under the most painstaking conditions of operation, it gave results too high by 10-15 per cent, and under less careful conditions was entirely misleading.
- <sup>6</sup> *J. Chem. Soc.* **1942**, p. 115.
- <sup>7</sup> The tendency of polyisoprenes to undergo substitution rather than addition under the action of halogens has been the subject of a separate investigation. No significant degree of substitutive reaction has been found to occur with iodine chloride under the conditions laid down by Kemp for iodine value determinations.
- <sup>8</sup> Kemp, *Ind. Eng. Chem.* **19**, 531 (1927); *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
- <sup>9</sup> Assay of well oxidized rubbers shows only very small ketone contents, which are simply accounted for by scission reactions.
- <sup>10</sup> The loss as shown in curve I of Figure 2 is of the correct order for loss due to spontaneous dehydration.
- <sup>11</sup> On the assumption that no chain scission, with accompanying consumption of oxygen in excess of 1 mol. to  $\overline{I}$  has occurred.
- <sup>12</sup> Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940).
- <sup>13</sup> Bolland and collaborators, *Trans. Inst. Rubber Ind.* **17**, 29 (1941).
- <sup>14</sup> Bolland, *Trans. Inst. Rubber Ind.* **16**, 267 (1941).
- <sup>15</sup> Kemp, Bishop and Lasselle, *Ind. Eng. Chem.* **23**, 1444 (1931).
- <sup>16</sup> *J. Chem. Soc.* **1942**, 115.
- <sup>17</sup> Since moisture hinders the addition of iodine chloride to the olefinic centers, it is desirable to prevent its entrance from the air, both in filling and in emptying the pipette.

# THE VAPOR-PRESSURE EQUATIONS OF SOLUTIONS AND THE OSMOTIC PRESSURE OF RUBBER\*

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## INTRODUCTION

1. The laws which are obeyed by ideally dilute and by perfect solutions have been obtained by Guggenheim<sup>1</sup>, and he has extended his analysis<sup>2</sup> to obtain the properties of a class of solutions to which the name regular<sup>3</sup> has been given. It is assumed that the solution consists of molecules of two types,  $\alpha$  and  $\beta$ , of approximately the same size, and that each molecule, whether of type  $\alpha$  or of type  $\beta$ , is surrounded by the same number  $z$  of other molecules, and the potential energy is regarded as the sum of contributions from each pair of molecules in direct contact. That is, the molecules are regarded as occupying sites on a regular lattice, and the potential energy arises from the interactions between molecules which occupy closest neighbor sites. Rushbrooke<sup>4</sup> has examined the properties of such a solution, using the Bethe method to set up the partition function for the assembly. The properties of solutions in which the molecules of one type are of such a size and shape that they have to be regarded as occupying two lattice sites have been investigated by Fowler and Rushbrooke<sup>5</sup>, who determined the limiting form of the vapor-pressure equations for extremely dilute and for extremely concentrated solutions. Chang<sup>6</sup> has determined, for a two-dimensional lattice, the value of the combinatory factor, which can be written as  $g_{2,1}(N_\alpha, N_\beta)$  for the case in which each molecule of type  $\alpha$  occupies two closest neighbor sites and each molecule of type  $\beta$  occupies one site. Chang's determination of  $g_{2,1}(N_\alpha, N_\beta)$  for a two-dimensional lattice is based on an analysis<sup>21</sup> of the corresponding adsorption problem, in which he superimposes some arbitrary assumptions on the Bethe method. It has, however, been shown<sup>7</sup> that the value which Chang obtained for  $g_{2,1}(N_\alpha, N_\beta)$  is applicable to two- and to three-dimensional lattices in which no two closest neighbors of a given site are also closest neighbors of one another. Fowler and Guggenheim<sup>8</sup> have shown how, once the combinatory factor has been evaluated, it can be used to determine the configurational entropy of mixing and thence the vapor-pressure equations when the energy of mixing is zero. Using Chang's value for  $g_{2,1}(N_\alpha, N_\beta)$ , they obtained for the vapor-pressure equations, when each solute molecule occupies two closest neighbor sites on the lattice and each solvent molecule occupies only one lattice site, the following equations:

$$\frac{p_\alpha}{[p_\alpha]_0} = \frac{N_\alpha(N_\alpha + \frac{1}{2}N_\beta)^{z-2}}{\{N_\alpha + \frac{1}{2}zN_\beta/(z-1)\}^{z-1}} \quad (1)$$

$$\frac{p_\beta}{[p_\beta]_0} = \frac{N_\beta(N_\beta + 2N_\alpha)^{\frac{1}{2}z-1}}{\{N_\beta + 2(z-1)N_\alpha/z\}^{\frac{1}{2}z}} \quad (2)$$

In these equations,  $p$  is the vapor pressure,  $N$  is the number of molecules of a particular species, and  $z$  is the coördination number of the lattice. The suffixes

\* Reprinted from the *Proceedings of the Cambridge Philosophical Society*, Vol. 39, Part 1, pages 54-67, 1943.

$\alpha$  and  $\beta$  denote the solute and solvent, respectively, and a symbol enclosed in square brackets with a subscript 0 refers to the pure species, while all the other symbols refer to the species in solution.

In the present paper, the vapor-pressure equations are obtained when each solute molecule consists of three groups (or submolecules) and occupies three sites on the lattice in such a way that successive groups in the molecule occupy closest neighbor sites on the lattice. The vapor-pressure equations which are obtained in this case are compared with those which are obtained when each solute molecule occupies two closest neighbor sites on the lattice, and the way in which the analysis can be generalized to the case in which the solute molecules are long-chain molecules is discussed. These results are then used to determine the variation of the osmotic pressure of a solution of long-chain polymer molecules in benzene or other solvent with the number of groups in the molecule, and also in terms of the concentration of the polymer. Expressions are also given for the entropy of mixing of solutions of molecules of different sizes.

#### THE VAPOR-PRESSURE EQUATIONS FOR THREE-GROUP SOLUTE MOLECULES

2. Let the number of distinguishable configurations of  $N_\alpha$  solute molecules, each of which consists of three groups and occupies three lattice sites in such a way that successive groups in the molecule occupy closest neighbor sites on the lattice, and of  $N_\beta$  solvent molecules, each of which occupies one lattice site, be  $g_{s,1}(N_\alpha, N_\beta)$ ; the value of  $g_{s,1}(N_\alpha, N_\beta)$  has been determined<sup>8</sup> by the author<sup>9</sup>, who has given an expression for  $\log g_{s,1}(N_\alpha, N_\beta)$  as a function of  $\theta$ , the fraction of the total number  $N_s$  of sites which are occupied by the three-group molecules. For the present purpose, it is convenient to rewrite these formulas in terms of  $N_\alpha$  and  $N_\beta$ . If we write  $\theta = \frac{3N_\alpha}{3N_\alpha + N_\beta}$ , so that

$1 - \theta = \frac{N_\beta}{3N_\alpha + N_\beta}$ , we get:

$$g_{s,1}(N_\alpha, N_\beta) = \left[ \frac{\{(3z - 4)N_\alpha z^{-1} + N_\beta\}!}{(3N_\alpha + N_\beta)!} \right]^{\frac{1}{2}} \frac{(3N_\alpha + N_\beta)!}{N_\alpha! N_\beta!} \left[ \frac{z(z-1)}{\sigma} \right]^{N_\alpha} \quad (3)$$

when the solute molecules are perfectly flexible, and

$$g'_{s,1}(N_\alpha, N_\beta) = \left[ \frac{\{(3z - 4)N_\alpha z^{-1} + N_\beta\}!}{(3N_\alpha + N_\beta)!} \right]^{\frac{1}{2}} \frac{(3N_\alpha + N_\beta)!}{N_\alpha! N_\beta!} \left( \frac{z}{\sigma} \right)^{N_\alpha} \quad (3')$$

when the molecules are completely inflexible. In particular, when the lattice is completely filled by three-group molecules, the number of configurations of these molecules on the lattice is given by:

$$\psi(3N_\alpha, 3) = \left[ \frac{\{(3z - 4)N_\alpha z^{-1}\}!}{(3N_\alpha)!} \right]^{\frac{1}{2}} \frac{(3N_\alpha)!}{N_\alpha!} \left[ \frac{z(z-1)}{\sigma} \right]^{N_\alpha} \quad (4)$$

when the molecules are perfectly flexible, and by:

$$\psi'(3N_\alpha, 3) = \left[ \frac{\{(3z - 4)N_\alpha z^{-1}\}!}{(3N_\alpha)!} \right]^{\frac{1}{2}} \frac{(3N_\alpha)!}{N_\alpha!} \left( \frac{z}{\sigma} \right)^{N_\alpha} \quad (4')$$

when the molecules are completely inflexible. Equations (34) and (40) of the earlier work<sup>8</sup> are asymptotic forms of Equations (4) and (4') above, and can be obtained from them by using Stirling's approximation.

The interaction energy of the assembly is:

$$\frac{1}{2}\{(3z-4)N_\alpha - N_{\alpha\beta}\}V_{\alpha\alpha} + N_{\alpha\beta}V_{\alpha\beta} + \frac{1}{2}(zN_\beta - N_{\alpha\beta})V_{\beta\beta} \quad (5)$$

where  $V_{\alpha\alpha}$ ,  $V_{\alpha\beta}$  and  $V_{\beta\beta}$ , respectively, are the interaction energies between solute-solute, solute-solvent and solvent-solvent pairs which occupy closest neighbor sites, interactions between more distant particles are neglected, and  $N_{\alpha\beta}$  is the number of solute-solvent pairs which occupy closest neighbor sites. We assume that the two types of molecules are so similar chemically that the energy of mixing is zero; this has the advantage of displaying the effect of the difference in size and shape of the two types of molecules for, if the energy of mixing is zero, any deviation from the laws of perfect solutions is due to the difference in size and shape of the two types of molecules. This condition is expressed by the equation:

$$2V_{\alpha\beta} = V_{\alpha\alpha} + V_{\beta\beta}, \quad (6)$$

so that in this case the interaction energy of the assembly reduces to:

$$\frac{1}{2}\{(3z-4)N_\alpha V_{\alpha\alpha} + zN_\beta V_{\beta\beta}\} \quad (7)$$

Thus condition (6) is the condition that the interaction energy of the assembly should be independent of  $N_{\alpha\beta}$ , the number of pairs of closest neighbor sites which are occupied by a molecule of type  $\beta$  and a submolecule of a molecule of type  $\alpha$ . The grand partition function of the assembly is therefore given by:

$$\Xi^{(l)} = \sum_{N_\alpha, N_\beta} g_{3,1}(N_\alpha, N_\beta) e^{-\frac{1}{2}\{(3z-4)N_\alpha V_{\alpha\alpha} + zN_\beta V_{\beta\beta}\}/kT} \times \{v_\alpha f_\alpha(T)\}^{N_\alpha} \{v_\beta f_\beta(T)\}^{N_\beta} \quad (8)$$

where

$$f_\alpha(T) = j_\alpha(T)(2\pi m_\alpha kT/h^2)^{\frac{3}{2}} \quad (9)$$

with a similar expression for  $f_\beta(T)$ ;  $j_\alpha(T)$  and  $j_\beta(T)$  are the partition functions for the internal degrees of freedom of solute and solvent molecules, respectively, and  $v_\alpha$  and  $v_\beta$  are the corresponding effective free volumes. The other symbols have their customary meanings.

In the usual way, the logarithm of the sum in Equation (8) can be replaced by the logarithm of the maximum term with only negligible error<sup>10</sup>. This term is denoted by  $\Xi^{(l)*}$  and is specified by the values  $N_\alpha^*$  and  $N_\beta^*$  of  $N_\alpha$  and  $N_\beta$ , respectively;  $N_\alpha^*$  and  $N_\beta^*$  are equal to the equilibrium values of  $N_\alpha$  and  $N_\beta$ . The Helmholtz free energy of the liquid phase is given by:

$$F^{(l)} = -kT \log \Xi^{(l)*} \quad (10)$$

It will be simpler to drop the asterisk in all the terms, but it must be understood that now  $N_\alpha$  and  $N_\beta$  refer to their values in the maximum term of  $\Xi^{(l)}$ , and which they assume at equilibrium. We can then write for the Helmholtz free energy of the liquid phase:

$$F^{(l)} = -kT \log g_{3,1}(N_\alpha, N_\beta) + \frac{1}{2}\{(3z-4)N_\alpha V_{\alpha\alpha} + zN_\beta V_{\beta\beta}\} - kT N_\alpha \log v_\beta f_\alpha(T) - kT N_\beta \log v_\beta f_\beta(T) \quad (11)$$

The Helmholtz free energy of the pure solute can be obtained from Equation (11) by putting  $N_\beta$  equal to zero, and this gives:

$$[F_\alpha^{(l)}]_0 = -kT \log \psi(3N_\alpha, 3) + \frac{1}{2}(3z-4)N_\alpha V_{\alpha\alpha} - kT N_\alpha \log v_\alpha f_\alpha(T) \quad (12)$$

Similarly, the Helmholtz free energy for the pure solvent can be obtained from Equation (11) by putting  $N_\alpha$  equal to zero, and this gives:

$$[F_\beta^{(l)}]_0 = \frac{1}{2}zN_\beta V_{\beta\beta} - kT N_\beta \log v_\beta f_\beta(T) \quad (13)$$

The Helmholtz free energy of mixing can be obtained from Equations (11), (12) and (13) and is given by:

$$(\Delta F)_{3,1} = F^{(l)} - [F_{\alpha}^{(l)}]_0 - [F_{\beta}^{(l)}]_0 = -kT \log \frac{g_{3,1}(N_{\alpha}, N_{\beta})}{\psi(3N_{\alpha}, 3)} \quad (14)$$

Equations (8), (11) and (12) apply to perfectly flexible molecules; if the molecules are completely inflexible  $g_{3,1}(N_{\alpha}, N_{\beta})$  in Equations (8) and (11) has to be replaced by  $g'_{3,1}(N_{\alpha}, N_{\beta})$  and  $\psi(3N_{\alpha}, 3)$  in Equation (12) has to be replaced by  $\psi'(3N_{\alpha}, 3)$ . However, since the ratio  $g_{3,1}(N_{\alpha}, N_{\beta})/\psi(3N_{\alpha}, 3)$  is the same as the ratio  $g'_{3,1}(N_{\alpha}, N_{\beta})/\psi'(3N_{\alpha}, 3)$ , it follows that Equation (14) applies whether the molecules are perfectly flexible or completely inflexible.

The difference between the chemical potential  $\mu_{\alpha}^{(l)}$  of the solute in the solution and its value  $[\mu_{\alpha}^{(l)}]_0$  for the pure solute at the same temperature and pressure is given by:

$$\mu_{\alpha}^{(l)} = [\mu_{\alpha}^{(l)}]_0 + \frac{\partial}{\partial N_{\alpha}} \left\{ -kT \log \frac{g_{3,1}(N_{\alpha}, N_{\beta})}{\psi(3N_{\alpha}, 3)} \right\} \quad (15)$$

The corresponding equation for the solvent species is:

$$\mu_{\beta}^{(l)} = [\mu_{\beta}^{(l)}]_0 + \frac{\partial}{\partial N_{\beta}} \left\{ -kT \log g_{3,1}(N_{\alpha}, N_{\beta}) \right\} \quad (16)$$

If we use the values of  $g_{3,1}(N_{\alpha}, N_{\beta})$  and of  $\psi(3N_{\alpha}, 3)$  given by Equations (3) and (4), or of  $g'_{3,1}(N_{\alpha}, N_{\beta})$  and of  $\psi'(3N_{\alpha}, 3)$  given by Equations (3') and (4'), we get:

$$\mu_{\alpha}^{(l)} = [\mu_{\alpha}^{(l)}]_0 + kT \log \frac{N_{\alpha}(N_{\alpha} + \frac{1}{3}N_{\beta})^{\frac{1}{2}z-3}}{\{N_{\alpha} + zN_{\beta}/(3z-4)\}^{\frac{1}{2}z-2}} \quad (17)$$

$$\mu_{\beta}^{(l)} = [\mu_{\beta}^{(l)}]_0 + kT \log \frac{N_{\beta}(N_{\beta} + 3N_{\alpha})^{\frac{1}{2}z-1}}{\{N_{\beta} + (3z-4)N_{\alpha}/z\}^{\frac{1}{2}z}} \quad (18)$$

The Helmholtz free energy of the vapor phase is given by:

$$\begin{aligned} \frac{F^{(v)}}{kT} = & -N'_{\alpha} \left[ \log \left\{ \left( \frac{2\pi m_{\alpha} kT}{h^2} \right)^{\frac{3}{2}} \frac{b_{\alpha}(T)V'}{N'_{\alpha}} + 1 \right\} \right. \\ & \left. - N'_{\beta} \left[ \log \left\{ \left( \frac{2\pi m_{\beta} kT}{h^2} \right)^{\frac{3}{2}} \frac{b_{\beta}(T)V'}{N'_{\beta}} \right\} + 1 \right] \right] \quad (19) \end{aligned}$$

where  $N'_{\alpha}$  and  $N'_{\beta}$ , respectively, are the numbers of solute and solvent molecules in the vapor phase of volume  $V'$ , and  $b_{\alpha}(T)$  and  $b_{\beta}(T)$ , respectively, are the partition functions for the rotations and internal vibrations of solute and solvent molecules in the vapor phase. The chemical potential of the species  $\alpha$  in the vapor phase is given by:

$$\mu_{\alpha}^{(v)} = -kT \log \left( \frac{2\pi m_{\alpha} kT}{h^2} \right)^{\frac{3}{2}} + kT \log \frac{p_{\alpha}}{kT} - kT \log b_{\alpha}(T) \quad (20)$$

where  $p_{\alpha}$  is the partial pressure of species  $\alpha$  in the vapor phase in equilibrium with the solution. If  $[p_{\alpha}]_0$  is the vapor pressure in equilibrium with the pure species  $\alpha$  under the same conditions, and  $[\mu_{\alpha}^{(v)}]_0$  is the corresponding chemical potential, then Equation (20) can be written in the form:

$$\mu_{\alpha}^{(v)} = [\mu_{\alpha}^{(v)}]_0 + kT \log \frac{p_{\alpha}}{[p_{\alpha}]_0} \quad (21)$$



In the same way, for the species  $\beta$ , we have the equation:

$$\mu_{\beta}^{(v)} = [\mu_{\beta}^{(v)}]_0 + kT \log \frac{p_{\beta}}{[p_{\beta}]_0} \quad (22)$$

If we equate the chemical potentials in the liquid and vapor phases we get the vapor-pressure equations:

$$p_{\alpha} = [p_{\alpha}]_0 \frac{N_{\alpha}(N_{\alpha} + \frac{1}{3}N_{\beta})^{\frac{1}{2}z-3}}{\{N_{\alpha} + zN_{\beta}/(3z-4)\}^{\frac{1}{2}z-2}} \quad (23)$$

$$p_{\beta} = [p_{\beta}]_0 \frac{N_{\beta}(N_{\beta} + 3N_{\alpha})^{\frac{1}{2}z-1}}{\{N_{\beta} + (3z-4)N_{\alpha}/z\}^{\frac{1}{2}z}} \quad (24)$$

The limiting forms of Equations (23) and (24) as  $z \rightarrow \infty$  are:

$$p_{\alpha} = [p_{\alpha}]_0 \frac{3N_{\alpha}}{3N_{\alpha} + N_{\beta}} e^{-2N_{\beta}/(3N_{\alpha} + N_{\beta})} \quad (25)$$

$$p_{\beta} = [p_{\beta}]_0 \frac{N_{\beta}}{3N_{\alpha} + N_{\beta}} e^{2N_{\alpha}/(3N_{\alpha} + N_{\beta})} \quad (26)$$

In Figures 1 and 2, the vapor-pressure curves are drawn, and show the

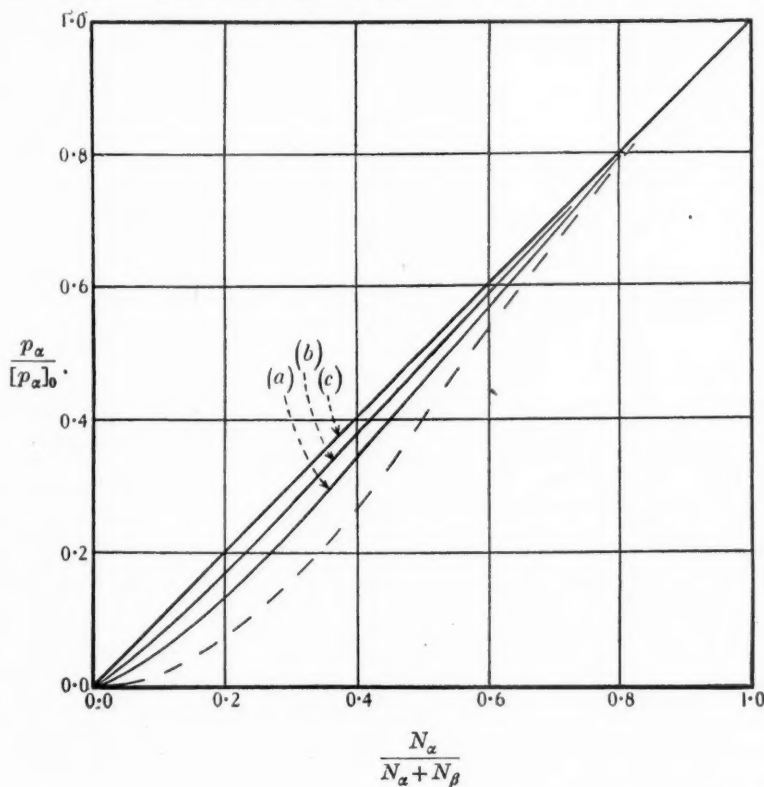


FIG. 1.—Vapor pressure of the solute (high polymer molecule) calculated for  $z = 8$ . Curves (a), (b) and (c) are drawn for  $n = 3, 2$  and  $1$ , respectively. The broken curve is for  $n = 10$ .

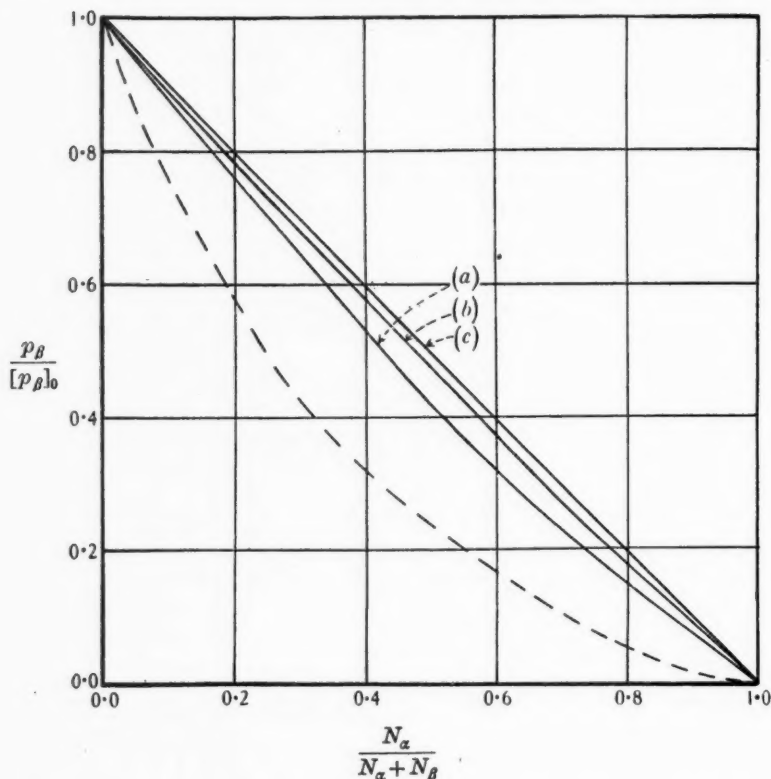


Fig. 2.—Vapor pressure of the solvent when the solute is a long-chain polymer, calculated for  $z = 8$ . The curves are drawn for the cases in which the polymer molecule contains two (curve (b)), three (curve (a)) and 10 (broken curve) submolecules.

vapor pressure plotted against the molar concentration of the solute. The values which have been plotted are those calculated for  $z = 8$ . Figure 1 shows the vapor pressure of the solute and Figure 2 that of the solvent. In each case, curve (a) gives the vapor pressure when each solute molecule contains three submolecules, curve (b) that when each solute molecule contains two submolecules and the straight line (c) is drawn to show the vapor pressure when the solute and solvent molecules are comparable in size and each molecule occupies only one site. These curves show the departures from Raoult's law, due to the differences in size and shape of the solvent and solute molecules.

The value of the combinatory factor which has been used in deriving Equations (23) and (24) was obtained on the assumption that no two closest neighbors of a given site are closest neighbors of one another, and so excludes the case of a close-packed lattice. Rushbrooke<sup>4</sup> has carried out calculations which indicate that, in the case of molecules of comparable size, each of which occupies one lattice site, close-packing of the molecules introduces no significant difference in the results, and it is unlikely to do so in the present case. If we compare the values collected in Table 1, some confirmation of this is obtained.

TABLE 1

VAPOR PRESSURE OF SOLUTE AND SOLVENT WHEN EACH SOLUTE MOLECULE CONSISTS OF THREE GROUPS AND OCCUPIES THREE LATTICE SITES. THE SUFFIX  $\alpha$  REFERS TO THE SOLUTE AND THE SUFFIX  $\beta$  TO THE SOLVENT

$\frac{N_\alpha}{N_\alpha + N_\beta}$	$pa/[pa]_0$				$p\beta/[p\beta]_0$			
	$z=4$	$z=6$	$z=8$	$z \rightarrow \infty$	$z=4$	$z=6$	$z=8$	$z \rightarrow \infty$
0.1	0.070	0.064	0.062	0.056	0.891	0.890	0.889	0.886
0.2	0.157	0.149	0.145	0.137	0.778	0.772	0.770	0.761
0.3	0.255	0.247	0.243	0.234	0.663	0.653	0.649	0.637
0.4	0.366	0.352	0.349	0.342	0.551	0.539	0.534	0.519
0.5	0.468	0.463	0.460	0.455	0.444	0.432	0.426	0.412
0.6	0.578	0.574	0.573	0.569	0.344	0.332	0.327	0.317
0.7	0.687	0.685	0.684	0.681	0.249	0.239	0.235	0.224
0.8	0.794	0.793	0.792	0.791	0.161	0.153	0.150	0.142
0.9	0.898	0.898	0.898	0.898	0.078	0.074	0.072	0.068

MOLECULES CONTAINING  $n$  SUBMOLECULES

3. If the vapor-pressure equations of solutions in which the solute molecules contain two and three submolecules are compared, the vapor-pressure equations when the solute molecules are long-chain molecules which contain  $n$  submolecules can be deduced by an immediate generalization. Suppose that each solute molecule contains  $n$  groups (or submolecules) and occupies  $n$  sites on the lattice in such a way that successive groups in the chain molecule occupy sites which are closest neighbors of one another. Let there be  $N_\alpha$  such solute molecules and  $N_\beta$  solvent molecules, each of which occupies one lattice site, so that the total number,  $N_s$ , of lattice sites is given by:

$$N_s = nN_\alpha + N_\beta \quad (27)$$

Denote by  $g_{n,1}(N_\alpha, N_\beta)$  the number of ways of arranging  $N_\alpha$  such solute molecules and  $N_\beta$  solvent molecules on the lattice of  $N_s$  sites. The determination of  $g_{n,1}(N_\alpha, N_\beta)$ , using the Bethe method in a similar way to that in which the corresponding quantities have been determined for two- and three-group solute molecules<sup>8</sup>, would require consideration of a group of sites large enough to accommodate the  $n$ -group molecule, with all its groups lying on a straight line through the central site. It is clearly impossible to formulate this problem in the general case; the enumeration of all possible configurations of two species of molecules of different sizes on a group of sites larger than the group which is sufficient for two- and three-group molecules is extraordinarily complicated.

If Equations (1) and (23) are compared, it can be seen that, in both cases, the numerical factor which multiplies  $N_\beta$  in the factor in the denominator is the ratio of the coordination number of the lattice to the number of sites which are closest neighbors of the sites which are occupied by a solute molecule when it lies along a straight line. In the general case, for an  $n$ -group solute molecule, this ratio is:

$$\frac{z}{2(z-1) + (n-2)(z-2)}$$

which can be more simply written as:

$$\frac{z}{nz - 2n + 2} \quad (28)$$

Furthermore, the factor in the numerator of the right-hand side of Equations (1) and (23) is raised to the power  $\frac{1}{2}z - 1$  multiplied by the number of groups contained in the solute molecule, while the factor in the denominator is raised to a power one greater than this. On the other hand, the factors on the right-hand sides of Equations (2) and (24) are raised to powers which are independent of the number of groups contained in each solute molecule<sup>11</sup>. This comparison leads us to write down the following equations for the vapor pressures when each solute molecule contains  $n$  submolecules and occupies  $n$  lattice sites in such a way that successive submolecules occupy closest neighbor sites while each solvent molecule occupies only one lattice site:

$$p_{\alpha} = [p_{\alpha}]_0 \frac{N_{\alpha} \{N_{\alpha} + N_{\beta}/n\}^{\frac{1}{2}nz-n}}{\{N_{\alpha} + zN_{\beta}/(nz-2n+2)\}^{\frac{1}{2}nz-n+1}} \quad (29)$$

$$p_{\beta} = [p_{\beta}]_0 \frac{N_{\beta} \{N_{\beta} + nN_{\alpha}\}^{\frac{1}{2}z-1}}{\{N_{\beta} + (nz-2n+2)N_{\alpha}/z\}^{\frac{1}{2}z}} \quad (30)$$

In the limit as  $z \rightarrow \infty$  these equations have the limiting forms:

$$p_{\alpha} = [p_{\alpha}]_0 \frac{nN_{\alpha}}{nN_{\alpha} + N_{\beta}} e^{-(n-1)N_{\beta}/(nN_{\alpha}-N_{\beta})} \quad (31)$$

$$p_{\beta} = [p_{\beta}]_0 \frac{N_{\beta}}{nN_{\alpha} + N_{\beta}} e^{(n-1)N_{\alpha}/(nN_{\alpha}+N_{\beta})} \quad (32)$$

The broken curves in Figures 1 and 2 show the vapor-pressure curves calculated from Equations (29) and (30) when  $n = 10$  for  $z = 8$ , and shows a considerable departure from Raoult's law represented by the straight lines.

The foregoing discussion also enables us to write expressions for the number of configurations of  $N_{\alpha}$  molecules of type  $\alpha$ , each of which contains  $n$  submolecules and occupies  $n$  sites on the lattice in such a way that successive submolecules occupy closest neighbor sites and of  $N_{\beta}$  molecules of type  $\beta$ , each of which occupies only one site on a lattice of  $nN_{\alpha} + N_{\beta}$  sites; for the case of completely inflexible molecules we obtain the result:

$$g'_{n,1}(N_{\alpha}, N_{\beta}) = \left[ \frac{\{(nz-2n+2)N_{\alpha}/z + N_{\beta}\}!}{\{nN_{\alpha} + N_{\beta}\}!} \right]^{\frac{1}{2}z} \times \frac{(nN_{\alpha} + N_{\beta})!}{N_{\alpha}!N_{\beta}!} \left( \frac{2}{\sigma} \right)^{N_{\alpha}} \left( \frac{1}{2}z \right)^{N_{\alpha}} \quad (33)$$

and, in particular, when the lattice is completely filled with the chain molecules, the number of configurations of these molecules on the lattice can be obtained from Equation (33) by putting  $N_{\beta}$  equal to zero, so  $N_s$  becomes equal to  $nN_{\alpha}$ . This gives the result:

$$\psi'(nN_{\alpha}, n) = \left[ \frac{\{(nz-2n+2)N_{\alpha}/z\}!}{(nN_{\alpha})!} \right]^{\frac{1}{2}z} \frac{(nN_{\alpha})!}{N_{\alpha}!} \left( \frac{2}{\sigma} \right)^{N_{\alpha}} \left( \frac{1}{2}z \right)^{N_{\alpha}} \quad (34)$$

and this is asymptotically equivalent to:

$$\left[ \frac{(nz-2n+2)^{\frac{1}{2}(nz-2n+2)} z}{n^{\frac{1}{2}(nz-1)} z^{\frac{1}{2}(nz-2n+2)}} \frac{z}{\sigma} \right]^{N_{\alpha}} \quad (35)$$

Equations (33) and (34) apply only to the case in which the chain molecules are constrained to lie along a straight line, that is, to the case in which they are

completely inflexible. We have seen that in the case of three-group molecules, the perfect flexibility of the molecules introduces into  $g_{3,1}(N_\alpha, N_\beta)$  a factor  $z - 1$  for each three-group molecule. In general, if the molecules are perfectly flexible, there will be introduced into  $g_{n,1}(N_\alpha, N_\beta)$  a factor for each long-chain molecule which depends on the number of submolecules and the geometry of the lattice. This, however, would only give the other limiting case of perfectly flexible molecules, contrasted with that of completely inflexible molecules to which Equations (33) and (34) apply. In general, the flexibility of the chain molecules will introduce into  $g_{n,1}(N_\alpha, N_\beta)$  a factor  $f^{N_\alpha}$ , where  $f$  depends on three considerations: (1) the number of submolecules in each chain molecule, (2) the configuration of the lattice, and (3) the degree of flexibility that is enjoyed by each chain molecule. When the chain molecules are flexible we can therefore write:

$$g_{n,1}(N_\alpha, N_\beta) = \left[ \frac{\{(nz - 2n + 2)N_\alpha/z + N_\beta\}!}{\{nN_\alpha + N_\beta\}!} \right]^{1/2} \times \frac{(nN_\alpha + N_\beta)!}{N_\alpha!N_\beta!} \left( \frac{2f}{\sigma} \right)^{N_\alpha} \left( \frac{1}{2}z \right)^{N_\alpha} \quad (36)$$

and, corresponding to this, we obtain:

$$\psi(nN_\alpha, n) = \left[ \frac{\{(nz - 2n + 2)N_\alpha/z\}!}{(nN_\alpha)!} \right]^{1/2} \frac{(nN_\alpha)!}{N_\alpha!} \left( \frac{2f}{\sigma} \right)^{N_\alpha} \left( \frac{1}{2}z \right)^{N_\alpha} \quad (37)$$

for the number of configurations when we have a lattice which is completely filled with chain molecules, provided only that the chain molecules are equally flexible whether they exist as a pure species or in solution.

It must, however, be emphasized that it is unnecessary to evaluate  $f$ , since its precise form is quite immaterial as far as the interesting thermodynamical quantities are concerned. The quantities, arising from the combinatory factor, with which we are concerned in determining the entropy of mixing and the vapor-pressure equations are  $\log \frac{g_{n,1}(N_\alpha, N_\beta)}{\psi(nN_\alpha, n)}$  and  $\frac{\partial}{\partial N_\beta} \log g_{n,1}(N_\alpha, N_\beta)$ , and it follows immediately from Equations (36) and (37) that these two quantities are necessarily independent of any factor which depends on the flexibility of the chain molecules, provided only that the chain molecules are equally flexible, whether they exist in solution or as a pure species. Since the flexibility necessarily depends on the steric properties of the molecules, this condition will probably always be fulfilled.

#### THE ENTROPY OF MIXING

4. When each solute molecule contains two groups and occupies two closest neighbor sites, while each solvent molecule occupies one site, Fowler and Guggenheim<sup>7</sup> have shown that the entropy of mixing is given by:

$$\frac{(\Delta S)_{2,1}}{k} = \{(z - 1)N_\alpha + \frac{1}{2}zN_\beta\} \log \frac{2(z - 1)N_\alpha z^{-1} + N_\beta}{2N_\alpha + N_\beta} - N_\alpha \log \frac{2N_\alpha}{2N_\alpha + N_\beta} - N_\beta \log \frac{N_\beta}{2N_\alpha + N_\beta} + (z - 1)N_\alpha \log \frac{z}{z - 1} \quad (38)$$

When each solute molecule consists of three groups and occupies three lattice sites, in such a way that successive groups occupy closest neighbor sites, and each solvent molecule occupies one site, the entropy of mixing can be deduced



immediately from Equations (3) and (4), or (3') and (4'), since for solutions of which the energy and volume of mixing are zero the entropy and free energy of mixing are connected by the relation:

$$\Delta F = T\Delta S$$

Thus<sup>12</sup>:

$$\frac{(\Delta S)_{n,1}}{k} = \log \frac{g_{n,1}(N_\alpha, N_\beta)}{\psi(nN_\alpha, n)} = \log \frac{g'_{n,1}(N_\alpha, N_\beta)}{\psi'(nN_\alpha, n)} \quad (39)$$

We therefore get:

$$\begin{aligned} \frac{(\Delta S)_{3,1}}{k} = & \frac{1}{2}z\{(3z-4)N_\alpha z^{-1} + N_\beta\} \log \frac{(3z-4)N_\alpha z^{-1} + N_\beta}{3N_\alpha + N_\beta} \\ & - N_\alpha \log \frac{3N_\alpha}{3N_\alpha + N_\beta} - N_\beta \log \frac{N_\beta}{3N_\alpha + N_\beta} + \frac{1}{2}(3z-4)N_\alpha \log \frac{3z}{3z-4} \end{aligned} \quad (40)$$

In a similar manner we can obtain from Equations (33) and (34), or (36) and (37), the entropy of mixing when each solute molecule contains  $n$  submolecules and occupies  $n$  lattice sites in such a way that successive submolecules occupy closest neighbor sites and each solvent molecule occupies one site. Independently of the flexibility of the chain molecules (subject only to the condition which was noted at the ends of § 3), the entropy of mixing is explicitly given by:

$$\begin{aligned} \frac{(\Delta S)_{n,1}}{k} = & \frac{1}{2}z\{(nz-2n+2)N_\alpha z^{-1} + N_\beta\} \log \frac{(nz-2n+2)N_\alpha z^{-1} + N_\beta}{nN_\alpha + N_\beta} \\ & - N_\alpha \log \frac{nN_\alpha}{nN_\alpha + N_\beta} - N_\beta \log \frac{N_\beta}{nN_\alpha + N_\beta} \\ & + \frac{1}{2}(nz-2n+2)N_\alpha \log \frac{nz}{nz-2n+2} \end{aligned} \quad (41)$$

#### THE OSMOTIC PRESSURE OF RUBBER SOLUTIONS

5. The osmotic pressure of a solution is related to the vapor pressure of the solvent in solution and that of the pure solvent by an equation which can be written<sup>13</sup>:

$$\int_0^\pi v_\beta d\pi = RT \log \frac{[p_\beta]_0}{p_\beta} \quad (42)$$

where  $v_\beta$  is the partial molar volume of the solvent,  $\pi$  is the osmotic pressure, and the other symbols have the same meanings as in the earlier sections of this paper. Posnjak<sup>14</sup> has shown that the volume of mixtures of rubber and benzene in which the volume fraction of benzene varied from 0.34 to 0.98 was within 1 per cent of the sum of the separate volumes of the rubber and of the benzene. Gee and Treloar<sup>15</sup> have obtained similar results in the range 0.012 to 0.332 of the weight fraction of benzene<sup>16</sup>. It follows that the partial molar volume of benzene in such mixtures is equal to the specific molar volume of pure benzene. We therefore assume that, throughout the range of concentrations to be considered,  $v_\beta$  is constant and equal to  $[v_\beta]_0$ , the specific molar volume of pure benzene. This gives:

$$\pi = \frac{RT}{[v_\beta]_0} \log \frac{[p_\beta]_0}{p_\beta} \quad (43)$$

for the osmotic pressure. For dilute solutions, this reduces to the well-known form<sup>17</sup>:

$$\pi = \frac{RT}{[v_\beta]_0} \cdot \frac{\Delta p_\beta}{[p_\beta]_0} \quad (44)$$

where  $\Delta p_\beta$  is the vapor-pressure lowering<sup>18</sup>.

From Equations (30) and (43), we get for the osmotic pressure of a solution of a long-chain polymer:

$$\pi = \frac{1}{2}z \frac{RT}{[v_\beta]_0} \log \frac{N_\beta + (nz - 2n + 2)N_\alpha/z}{N_\beta + nN_\alpha} - \frac{RT}{[v_\beta]_0} \log \frac{N_\beta}{N_\beta + nN_\alpha} \quad (45)$$

Expansion of the log terms of Equation (45), neglecting terms beyond the second, leads to the expression:

$$\pi = \frac{RT}{[v_\beta]_0} \left[ \frac{1}{n} \left( \frac{nN_\alpha}{N_\beta + nN_\alpha} \right) + \left\{ \frac{1}{2} - \frac{1}{z} \left( 1 - \frac{1}{n} \right)^2 \right\} \left( \frac{nN_\alpha}{N_\beta + nN_\alpha} \right)^2 + \dots \right] \quad (46)$$

Now  $\frac{nN_\alpha}{N_\beta + nN_\alpha} = v_r$ , the volume fraction of rubber in the solution. Further, if  $V_r$  is the partial molar volume of the rubber in the solution, then  $N = V_r/[v_\beta]_0$ , and Equation (1) becomes:

$$\pi \simeq RT \left[ \frac{v_r}{V_r} + \left( \frac{1}{2} - \frac{1}{z} \right) \frac{v_r^2}{[v_\beta]_0} \right] \quad (47)$$

If  $c$  is the concentration of the solution (grams per cc.) and  $\rho_r$ ,  $M_r$  are the density and molecular weight of the rubber, we may write (2) in the form:

$$\frac{\pi}{c} \simeq \frac{RT}{M_r} + \left( \frac{1}{2} - \frac{1}{z} \right) \frac{RT}{\rho_r^2 [v_\beta]_0} c \quad (48)$$

This is in agreement with the form of equation given by Flory<sup>19</sup> and Huggins<sup>20</sup>, differing only in the coefficient of the quadratic term.

To the same degree of approximation, the vapor pressure of a dilute solution is obtained by combining the above result with Equation (44) of the paper, giving:

$$\frac{\Delta p_\beta}{[p_\beta]_0} = \frac{[v_\beta]_0}{M_r} c + \left( \frac{1}{2} - \frac{1}{z} \right) \frac{[v_\beta]_0}{\rho_r^2} c^2 \quad (49)$$

#### SUMMARY

6. Assuming that the solute and solvent molecules in a solution can be regarded as occupying sites on a regular lattice and that the potential energy arises from interactions between molecules which occupy closest neighbor sites, the vapor-pressure equations have been determined for solutions in which each solute molecule contains three groups (or submolecules) and occupies three lattice sites in such a way that successive submolecules occupy closest neighbor sites on the lattice, while each solvent molecule occupies only one site. The vapor-pressure equations are compared with those which have already been obtained by Fowler and Guggenheim for the case in which each solute molecule contains two submolecules to determine the effect on the form of the vapor-

pressure equations of the number of submolecules in each solute molecule. This enables the determination of the vapor-pressure equations when each solute molecule contains  $n$  submolecules and occupies  $n$  lattice sites in such a way that successive submolecules occupy closest neighbor sites on the lattice. In this latter case the vapor-pressure equations are:

$$p_{\alpha} = [p_{\alpha}]_0 \frac{N_{\alpha} \{N_{\alpha} + N_{\beta}/n\}^{\frac{1}{2}nz-n}}{\{N_{\alpha} + zN_{\beta}/(nz - 2n + 2)\}^{\frac{1}{2}nz-n+1}},$$

$$p_{\beta} = [p_{\beta}]_0 \frac{N_{\beta} \{N_{\beta} + nN_{\alpha}\}^{\frac{1}{2}z-1}}{\{N_{\beta} + (nz - 2n + 2)N_{\alpha}/z\}^{\frac{1}{2}z}}$$

These equations are used to determine the osmotic pressure of solutions of long-chain polymers, and it is found that in the region of osmotic interest, the osmotic pressure is given by an equation of the form:

$$\pi = \frac{A_1 c}{1 - A_2 c}$$

where  $c$  grams of solute per 100 cc. of solution is the concentration. It is shown that this equation can be written approximately:

$$\pi = A_1 c(1 + A_2 c)$$

which is the quadratic relation which has usually been fitted to osmotic measurements. To this approximation  $\pi/c$  plotted as a function of  $c$  gives a straight line of which the intercept on the  $\pi/c$  axis determines the molecular weight of the polymer molecule and the gradient determines the number of submolecules in each polymer molecule.

In the course of the investigation it is found that the entropy of mixing of  $N_{\alpha}$  polymer molecules (of the kind specified above), each of which contains  $n$  submolecules and of  $N_{\beta}$  solvent molecules, each of about the same size as a submolecule of the polymer is given by:

$$\begin{aligned} \frac{(\Delta S)_{n,1}}{k} = & \frac{1}{2}z \{ (nz - 2n + 2)N_{\alpha}z^{-1} + N_{\beta} \} \log \frac{(nz - 2n + 2)N_{\alpha}z^{-1} + N_{\beta}}{nN_{\alpha} + N_{\beta}} \\ & - N_{\alpha} \log \frac{nN_{\alpha}}{nN_{\alpha} + N_{\beta}} - N_{\beta} \log \frac{N_{\beta}}{nN_{\alpha} + N_{\beta}} \\ & + \frac{1}{2}(nz - 2n + 2)N_{\alpha} \log \frac{nz}{nz - 2n + 2} \end{aligned}$$

#### ACKNOWLEDGMENT

I would like to thank J. K. Roberts for suggesting this problem. The investigation described in this paper forms part of the program of fundamental research on the properties of rubber undertaken by the British Rubber Producers' Research Association, whom the author wishes to thank for the grant of a research scholarship. The work described in this paper was completed in June 1941, but its earlier publication has been prevented by the concentration of the author on other war research.

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- <sup>2</sup> Guggenheim, *Proc. Roy. Soc. (London)* **A148**, 304 (1935).
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- <sup>6</sup> Chang, *Proc. Cambridge Phil. Soc.* **35**, 293 (1939).
- <sup>7</sup> Fowler and Guggenheim, "Statistical Mechanics", Cambridge, England, 1939, Sec. 821.
- <sup>8</sup> Miller, *Proc. Cambridge Phil. Soc.* **38**, 109 (1942).
- <sup>9</sup> In this work, I used  $g_3(N_\alpha, \frac{1}{2}N_\beta)$  to denote the combination factor which I now prefer to denote by  $g_{3,1}(N_\alpha, N_\beta)$ , since this provides a more informative notation, capable of greater useful generalization. Also, the following misprints in the earlier work (*Proc. Cambridge Phil. Soc.* **38**, 109 (1942)) should be noted. The curly bracket on the right-hand side of Equation (1) should be raised to the power  $\frac{1}{2}N_\alpha$ ; in Equation (12) there should be a minus sign before the term on the right-hand side; and the last term on the right-hand side of Equation (13) should be  $-\frac{1}{2} \log (z - \theta)$ .
- <sup>10</sup> Fowler, "Statistical Mechanics", Cambridge, England, 1936, Sec. 541.
- <sup>11</sup> Since Equations (2) and (24) give the vapor pressure of the solvent species, this result is to be expected.
- <sup>12</sup> Compare Equation (14).
- <sup>13</sup> Guggenheim, "Modern Thermodynamics", Methuen, 1935, p. 85. Equation (425).
- <sup>14</sup> Posnjak, *Kolloidchem. Beih.* **3**, 417 (1912).
- <sup>15</sup> Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942).
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- <sup>17</sup> Falkenhagen, "Electrolytes", translated by R. P. Bell, Oxford, England, 1934.
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## INTERACTION BETWEEN RUBBER AND LIQUIDS

### IV. FACTORS GOVERNING THE ABSORPTION OF OIL BY RUBBER \*

G. GEE

A piece of vulcanized rubber, dropped into benzene, swells to several times its size but retains its shape. With raw rubber, a further stage ensues, in which the rubber flows and ultimately disperses. Inevitably, one tends to form a picture of the rubber attracting and holding the liquid with some strong force. It is the purpose of this paper to explain why this picture is believed to be entirely false, and to give an alternative explanation of the phenomena of swelling and solution.

It will be necessary first to consider briefly the way in which simpler materials mix with one another. The simplest possible system is that of two gases which do not react with each other. In a gas the molecules spend most of their time a long way from one another, and the total energy of the system is therefore made up largely of the kinetic energy of thermal motion. As a consequence of this kinetic energy the gas molecules tend, on the average, to distribute themselves uniformly, so that any pair of gases mix completely. A quantitative interpretation can be given to this mixing tendency, in terms of the concept of entropy. Of the various ways in which entropy may be regarded, the most useful for the present purpose is in terms of probability. Qualitatively it is evident that gas molecules in violent thermal agitation are extremely unlikely to arrange themselves so all molecules of one type are confined to one part of the vessel. This is expressed in thermodynamic language by saying that the entropy of such an arrangement would be small. The second law of thermodynamics states that if, as in a gas, there is no change of energy, a system tends to take up the state of maximum entropy, or maximum randomness. A quantitative expression to the relationship between the entropy  $S$  and probability  $W$ , takes the form:

$$S = k \log_e W \quad (1)$$

where  $k$  is Boltzmann's constant. The use of this equation may be illustrated by calculating the increase of entropy on mixing 4 molecules of gas A with 4 of gas B. Suppose initially that the four A molecules are confined to a vessel divided into four cells, each of which contains one molecule. The number of ways of arranging the molecules in the cells will be  $4!$ . Further, the 4 B molecules may be arranged in  $4!$  ways in a similar vessel, so that the total number of ways of arranging the 8 without allowing them to mix is  $(4!)^2$ . If, now, the A and B molecules are distributed at random among the eight cells, the total number of arrangements is  $8!$ . Hence, by Equation (1), the increase of entropy  $\Delta S^m$  on mixing is:

$$\Delta S^m = k (\log_e 8! - \log_e (4!)^2) = k \log_e 70$$

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This quantity, usually known as the entropy of mixing, is a measure of the tendency of the molecules to mix. The calculation may be generalized for large numbers of molecules, leading to the result that the increase of entropy  $\Delta S^m$  on mixing  $N_1$  gram mols of type 1 with  $(1 - N_1)$  gram-mols of type 2 is given by:

$$\Delta S^m = R \{ N_1 \log_e 1/N_1 + (1 - N_1) \log_e 1/(1 - N_1) \} \quad (2)$$

The next case to be considered is that of the mixing of 2 liquids, and here another factor becomes important. The molecules of a liquid are close together and therefore exert strong forces on one another. This is the origin of the latent heat of evaporation, which represents the work done in overcoming the cohesive energy of the molecules. As different liquids do not have the same molar latent heats, it must be concluded that their molecules cohere with different energies. This difference depends partly on the chemical nature of the molecules and partly on the way they pack together.

A typical molecule in the liquid may be regarded as surrounded by a number,  $Z$ , say, of similar molecules, each of which exerts an attractive force on it. This force is equivalent to a bond, whose energy depends on the nature of the molecules and on their distance apart. Now to mix two liquids, 1 and 2, it is necessary to break some of the 1-1 and 2-2 bonds, at the same time producing 1-2 bonds. A typical molecule 1 will still be surrounded by  $Z$  other molecules, but these will not all be 1 molecules but, on the average, will consist of  $v_1 Z 1$  molecules and  $v_2 Z 2$  molecules where  $v_1$  and  $v_2$  are the volume fractions of 1 and 2 in the mixture. Now the cohesive energy of 1 cc. of liquid is made up of the sum of the energies of all the bonds between the molecules in the liquid. It is clear that the cohesive energy of a mixture will not, in general, be equal to the sum of the cohesive energies of its separated components. It would be easy to calculate, on the above basis, what the cohesive energy would be if we knew how the energy  $e_{12}$  of a 1-2 bond was related to the energies  $e_{11}$  and  $e_{22}$  of 1-1 and 2-2 bonds. Hildebrand<sup>1</sup> has suggested that  $e_{12} = \sqrt{e_{11}e_{22}}$  and has shown that, on this basis, the increase of energy  $\Delta E$  on mixing is given by:

$$\Delta E = v_1 v_2 \left( \sqrt{\frac{E_1}{V_1}} - \sqrt{\frac{E_2}{V_2}} \right)^2 \text{ cal. per cc. of mixture} \quad (3)$$

where  $E_1/V_1$  and  $E_2/V_2$  are the cohesive energy densities (C.E.D.) of the two liquids [ $E$  = latent heat of evaporation at constant volume in calories per mol,  $V$  = mol. vol. (c.c.s.)]. This increase of energy has to be supplied at the expense of thermal energy, so heat is absorbed and a fall of temperature is observed. There are of course exceptions to this; some pairs of liquids, *e.g.*, acetone and chloroform, evolve heat on mixing. This means that the 1-2 bonds are stronger than the 1-1 and 2-2 bonds they replace. In other words, there has been some form of association between the components; heat evolved on mixing is in fact to be regarded as a heat of reaction.

The mixing of liquids is thus accompanied in general by two changes: (1) an increase of entropy which tends to make them mix; and (2) an absorption of heat, which represents energy which has to be supplied before mixing is possible. These factors are in opposition, and to discover their joint effect it is necessary to introduce the concept of free energy. This is best regarded for the present purpose as a chemical potential. Just as the temperatures of two bodies determine the direction in which heat will flow, so the free energies of two systems determine the direction of chemical reaction or mixing. Two

liquids will mix only as long as this process involves a decrease of free energy. Now, writing  $\Delta H$  for the increase of energy,  $\Delta G$  for the increase of free energy and  $T$  for the absolute temperature, it is known that:

$$\Delta G = \Delta H - T\Delta S$$

Hence, liquids will mix as long as  $\Delta G$  is negative, *i.e.*,  $T\Delta S > \Delta H$ . For simple liquids, the entropy of mixing has the same value as given above for gases, while  $\Delta H$  is roughly related to the difference between the C.E.D.'s of the liquids. Thus, liquids which are only partially miscible are in general those having different C.E.D.'s; liquids of similar C.E.D. are miscible in all proportions.

Now rubber, from the standpoint of solubility, is a liquid. This may seem surprising, but its mechanical properties make it clear that the rubber molecules have a good deal of freedom to slip past one another, which is just the characteristic that is associated with the liquid state. This of course is not a complete description of rubber, but it represents the factor which is important for the present purpose. The absorption of oil by rubber is thus to be regarded as the mixing of two liquids, rubber and oil. The problem to be solved is whether these liquids mix because of the increase of entropy or whether there is really some force of attraction between the rubber and the oil. The fact that mixing occurs means that  $\Delta G$  is negative, though it gives no indication of its magnitude. Nor can  $\Delta G$  be calculated from measurements of the extent or rate of swelling of rubber in a liquid, and this is usually the only information available. It can, however, be obtained from the vapor pressures of the oil when pure and when mixed with rubber. It is not difficult to see that there should be a relationship between vapor pressure and free energy, for the condition which has to be satisfied before rubber will imbibe more oil can be stated in alternative ways, either the imbibition must be accompanied by a decrease of free energy, or the vapor pressure of the pure oil must be greater than its vapor pressure above the rubber. The determination of  $\Delta G$  can, therefore, be reduced experimentally to the measurement of vapor pressures. This is simpler in theory than in practice but, with care, accurately reproducible results can be obtained.

A detailed study of the system rubber and benzene has been described by Gee and Treloar<sup>2</sup>. To cover the whole range of composition, four different experimental methods were needed; the fact that these gave a continuous variation of vapor pressure with composition is a good test of their reliability. All pressures measured were shown to be true equilibrium values, from which  $\Delta G$  could be calculated.

The heat of swelling  $\Delta H$  could in principle be measured in a calorimeter, but the slowness with which rubber swells makes this very difficult experimentally. Another method is to calculate  $\Delta H$  from values of  $\Delta G$  at two different temperatures. The result depends on a small difference between two large values of  $\Delta G$ , and therefore demands the highest order of accuracy in measuring vapor pressure. Nevertheless, it can be done, and although one cannot claim to obtain  $\Delta H$  with high relative accuracy, the results leave no doubt as to its sign and order of magnitude. Given  $\Delta G$  and  $\Delta H$ ,  $T\Delta S$  is obtained by difference.

The results obtained by this method for the system, rubber + benzene, are shown in Figure 1.

What are the conclusions from this work? First of all, that the picture

of rubber offering a strong attraction to the oil is completely wrong. Any such attraction would mean that  $\Delta H$  would be negative, and it is found to be positive. Secondly, that the true explanation of the imbibition of oil by rubber is the same phenomenon that underlies the mixing of simple gases and liquids, namely, an increase in entropy brought about by the natural tendency of the molecules to mix by thermal motion. The fact that the phenom-

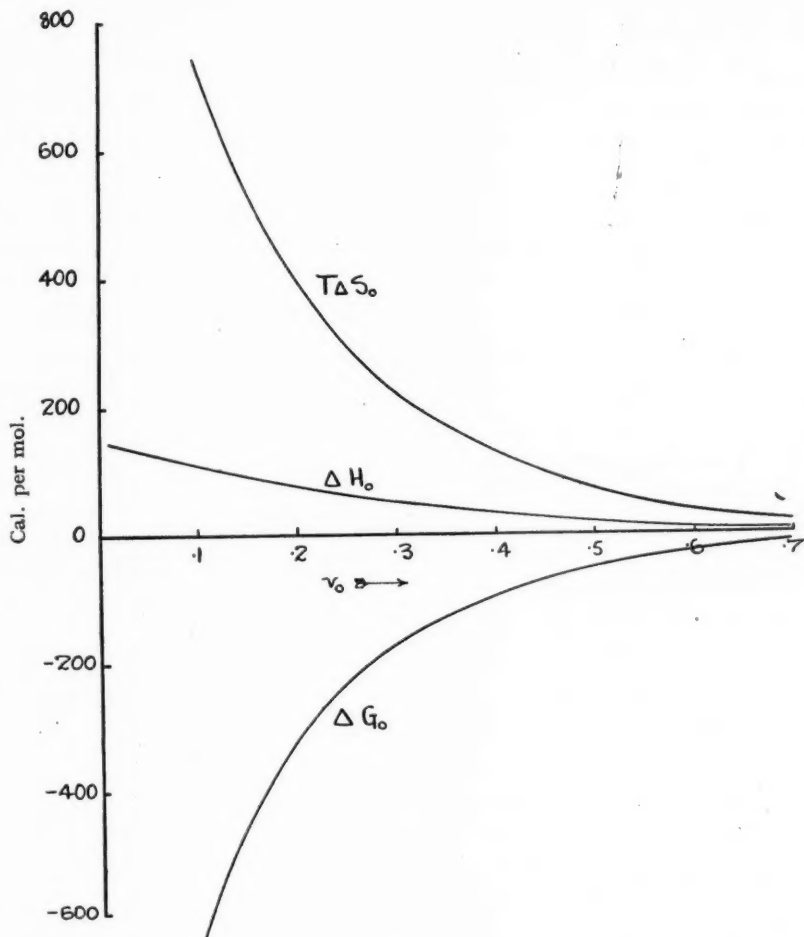


FIG. 1.

enon of swelling is observed has nothing to do with any attractive forces between rubber and oil; it is rather a visual indication of the extent to which the rubber molecules themselves cohere. Treloar<sup>3</sup> has shown that, to explain the mechanical behavior of raw rubber, the rubber molecules must be, for the most part, free to slide over one another like the molecules of a liquid, yet at certain points sufficiently strongly attached to withstand a tension. This

attachment has been explained as an entanglement of the rubber molecules, the probability of which increases greatly with their length. Thus, only high molecular raw rubber shows either elastic retraction or swelling as a prelude to dissolution.

Further consideration of the vapor pressure data reveals another surprising fact. The heat of mixing of rubber and benzene seems small when expressed in terms of 1 gram of rubber. But in terms of the rubber molecule it becomes large; to dissolve 1 gram-molecule of raw rubber in benzene, something like 500,000 calories of energy have to be provided. Now this is far more than can be compensated for by the increase of entropy calculated on the basis described above. Indeed the measured entropy of swelling is as much as 1,000 times that calculated on this basis. An explanation of this discrepancy has recently been given in a theory which treats the rubber molecule as made up of small units, each of the same size as the solvent molecule. It is easy to see how the error arises by using the same method as before to calculate the increase of entropy on mixing four small molecules with one flexible molecule four times the size. According to the theory developed above, the number of arrangements before mixing would be  $4! \times 1!$ , and after mixing  $5!$ , so that the entropy of mixing would be  $k \log_e \frac{5!}{4!} = k \log_e 5$ . This calculation involves the assumption

that the large molecule could be accommodated in the same space as a small one, which is evidently untrue. It is clear that the large molecule requires four adjacent cells, and a revision of the calculation bearing this in mind leads to a considerably larger entropy of mixing. Extended to the long rubber molecule, this analysis accounts quantitatively for the very large entropy of swelling of rubber in benzene<sup>4</sup>.

*The swelling of rubber in different liquids.*—How far can these ideas be extended to explain why some liquids are absorbed by rubber much more readily than others? The only systems which have been properly studied by these methods are rubber plus benzene and rubber plus methyl alcohol. These, however, show clearly the main factors by which the swelling will be determined. It is evident that the above explanation of the large entropy of mixing does not depend on any special assumptions about the nature of the liquid and, in general, the entropy of mixing must be expected to be large and more or less independent of the liquid. The heats of swelling of rubber by various liquids may, however, differ widely, and it is on this factor that the explanation of the different swelling powers of liquids must be based.

Consider a piece of rubber swollen to a certain extent by a liquid, and immersed in more of the same liquid. Imbibition of more liquid would be assisted by the entropy increase  $\Delta S_0$ , but resisted by the heat absorption  $\Delta H_0$ . If  $\Delta G_0$  is negative, i.e.,  $T\Delta S_0 > \Delta H_0$ , more liquid will be absorbed, and the process will continue either until the rubber is dissolved or until a point is reached at which  $\Delta G_0 = 0$ . Now the heat of dilution  $\Delta H_0$  is approximately proportional to the square of the rubber concentration  $C$ , so that  $\Delta H_0/C^2$  is independent of the degree of swelling  $Q$  (cc. of liquid per 1 gram of rubber). This is represented in Figure 2 by a series of horizontal lines, each characteristic of one liquid. As  $\Delta S_0$  is independent of the nature of the liquid, a single curve of  $\frac{T\Delta S_0}{C^2} \sim Q$  can also be drawn in Figure 2. The curve drawn is for a vulcanized rubber, and lies somewhat below that for raw rubber (for which  $\Delta S_0 > 0$  for all values of  $Q$ ). When this curve cuts the  $\Delta H_0/C^2$  line for a given liquid,

$T\Delta S_0 = \Delta H_0$  and  $\Delta G_0 = 0$  for that liquid; the corresponding value of  $Q$  is the equilibrium degree of swelling of the rubber in that liquid.

Now the description given of the mixing of simple liquids relates  $\Delta H_0$  to the difference between the C.E.D.'s of the liquids. Hence vulcanized rubber should swell to its greatest extent in a liquid having the same C.E.D. as itself and a plot of  $Q$  in a series of liquids against the C.E.D.'s of the liquids should give a curve with a maximum. Examination of Whitby's extensive data<sup>5</sup> shows this to be roughly true, although many individual discrepancies remain to be explained.

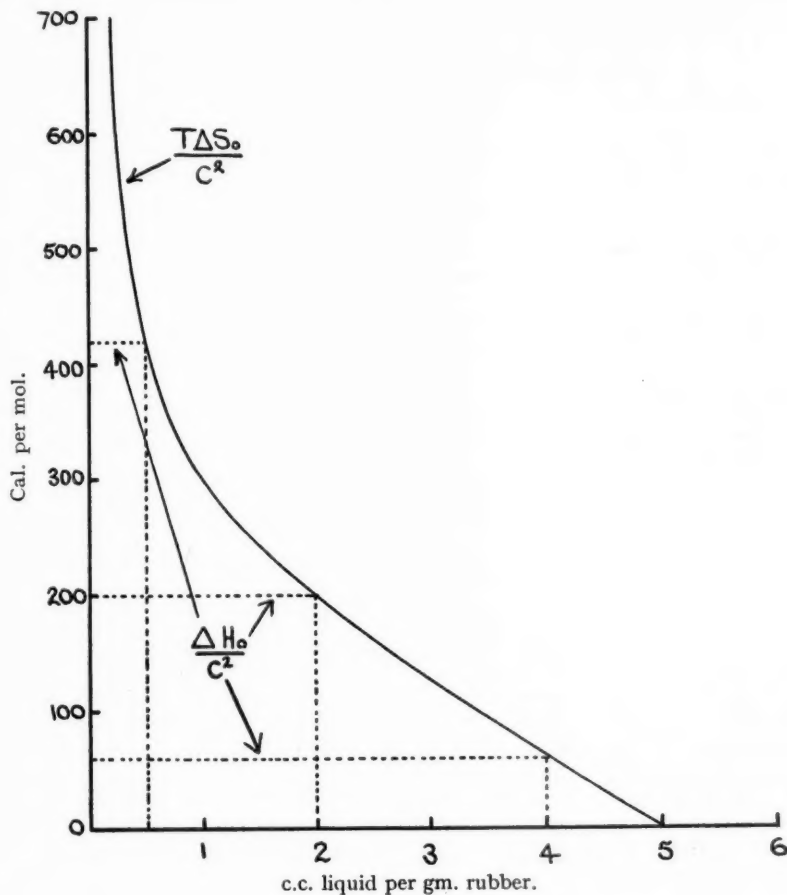


FIG. 2.

A more complete theory<sup>6</sup> shows that the molecular volume  $V_0$  of the liquid is also important, and that the swelling  $Q$  should be a function of  $\sqrt{V_0} \left( \sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_r}{V_r}} \right)$ , where the suffix  $r$  refers to rubber. The C.E.D. of a liquid is easily found from its latent heat of evaporation, but this method



cannot be applied to rubber. It should, however, be possible to estimate  $E_r/V_r$  for a sample of rubber from its swelling in a series of liquids of known C.E.D. If the swelling of a vulcanized rubber is measured in a series of liquids covering as continuously as possible a range of C.E.D., the C.E.D. of the liquid in which the swelling is a maximum will be approximately equal to that of the rubber. This principle can be refined by using a mathematical method to locate the exact position of the maximum of the swelling  $\sim$  C.E.D. curve (see Appendix).

Some experiments have been made along these lines, using a range of 20 aliphatic liquids with C.E.D. values ranging from 50 calories per cc. (*n*-pentane)

TABLE 2  
RUBBER COMPOUNDS USED IN SWELLING MEASUREMENTS

Materials	Parts by wt. in compound				
	1	2	3	4	5
Smoked sheet	100	100	100	100	100
Sulfur	3.5	3	3	3	3
Zinc oxide	6	5	5	100	18
Stearic acid	0.5	3	3	2.5	1.5
Mercaptobenzothiazole	0.5	1	1	...	1
Carbon black	...	45	100	...	...
Nonox-S	...	1.5	1.5	1	1
Pine tar	...	1	2	...	3.5
Tetramethylthiuram disulfide	...	...	0.1	1	...
Magnesium carbonate	...	...	...	50	42
Mineral oil	...	...	...	5	...
Magnesium oxide	...	...	...	...	4
Red oxide	...	...	...	...	14
Lithopone	...	...	...	...	64
Paraffin wax	...	...	...	...	1.5
Total	110.5	159.5	215.6	262.5	253.5

TABLE 3  
SWELLING OF NATURAL RUBBER COMPOUNDS

Liquid	$\sqrt{\frac{E_0}{V_0}}$	Q				
		1	2	3	4	5
<i>n</i> -Pentane	7.07	2.05	1.67	1.12	1.70	...
<i>n</i> -Hexane	7.40	2.77	2.06	1.21	2.12	2.38
<i>n</i> -Heptane	7.50	3.00	2.33	1.43	2.22	2.50
Ethyl ether	7.60	2.79	1.96	1.46	1.88	2.35
Isobutyl <i>n</i> -butyrate	7.78	3.43	2.33	1.59	2.72	2.92
<i>n</i> -Butyl <i>n</i> -butyrate	8.06	3.57	2.50	1.68	3.10	2.14
<i>n</i> -Butyl acetate	8.53	2.48	2.31	1.35	1.89	2.23
<i>n</i> -Propyl acetate	8.75	1.71	1.45	1.12	1.45	1.59
Ethyl acetate	9.08	0.89	0.76	0.70	0.74	0.86
Ethyl formate	9.43	0.38	0.36	0.39	0.35	0.37
Methyl acetate	9.58	0.31	0.29	0.34	0.27	0.30
Methyl formate	10.16	0.04	0.11	0.16	0.12	0.13
Diisopropyl ketone	8.08	4.05	2.02	1.30	2.10	2.43
Ethylmethyl ketone	9.22	0.64	0.58	0.58	0.56	0.63
Acetone	9.77	0.19	0.15	0.19	0.14	0.15
Butylaldehyde	9.00	1.54	1.28	0.97	1.50	1.33
<i>n</i> -Capronitrile	9.19	0.85	0.76	0.71	0.73	0.85
Propionitrile	10.68	0.07	0.06	0.10	0.06	0.06
Acetonitrile	11.89	0.02	0.02	0.05	0.02	0.02
C.E.D. of rubber	...	63.7	64.0	64.0	63.7	63.7

to 141 calories per cc. (acetonitrile). Details of these liquids, and the method of evaluating their C.E.D.'s, are given in Appendix 2. The swelling of a series of vulcanized natural rubber compounds was then measured in the following way. The rubbers were in the form of sheets about 2 mm. thick; samples about 1 cm. square were cut, weighed and allowed to swell for three days in the selected liquids. After removing excess liquid with filter paper, the rubber was then reweighed, and the gain in weight used to calculate the swelling, expressed as cc. of liquid imbibed per gram of actual rubber in the compound. This method of course eliminates any purely diluent effect of the fillers. Subsidiary experiments showed that the absorption of liquid after 3 days was a reasonable measure of the equilibrium swelling. Table 2 gives details of the rubber compounds used, and Table 3 records the swelling data.

All compounds were vulcanized for 30 minutes at 40 lbs. steam.

Table 3 also includes values for the C.E.D.'s of the rubbers, obtained by

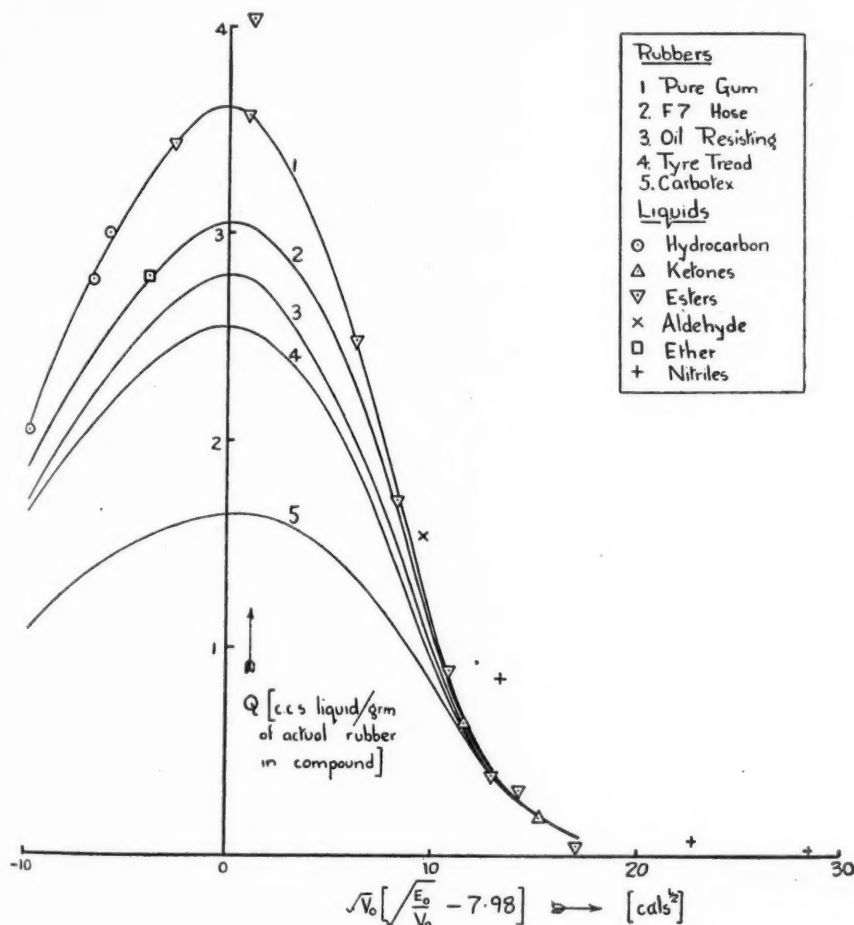


FIG. 3.

the method of Appendix 1. Figure 3 gives a plot of the swelling  $Q$  of these compounds as a function of  $\sqrt{V_0} \left( \sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_r}{V_r}} \right)$ . For the sake of clarity, experimental points are given only for rubber 1, but similar agreement is found for the other rubbers. Several conclusions may be drawn from Figure 3.

The swelling is determined, within this range of liquids, by the value of the function  $\sqrt{V_0}(\sqrt{E_0/V_0} - \sqrt{E_r/V_r})$ . The theory is thus confirmed by these results.

The C.E.D. of the rubber is unaffected by compounding. The absolute swelling of a rubber in a good swelling agent is reduced by a reinforcing filler. As no comparable reduction occurs for a bad swelling agent, it appears likely that the effect of the filler is to link the rubber chains together, so as to restrict their maximum distension. It is consistent with this view that no comparable effect is found with non-reinforcing fillers.

*Synthetic rubbers.*—The same considerations may be applied to the problem of the swelling of different rubbers. These will in general have different C.E.D.'s and will, therefore, show their maximum swelling in different liquids: this is known to be the case. A quantitative study has been made by using the above series of liquids as swelling agents for the rubbers compounded according to Table 5. The experimental method was the same as for the natural rubber compounds: the results are given in Table 6.

If the theory is correct, the different swelling behavior of these rubbers should be associated with differences in their C.E.D.'s. This is shown to be the case by Table 4 and Figures 4 to 8.

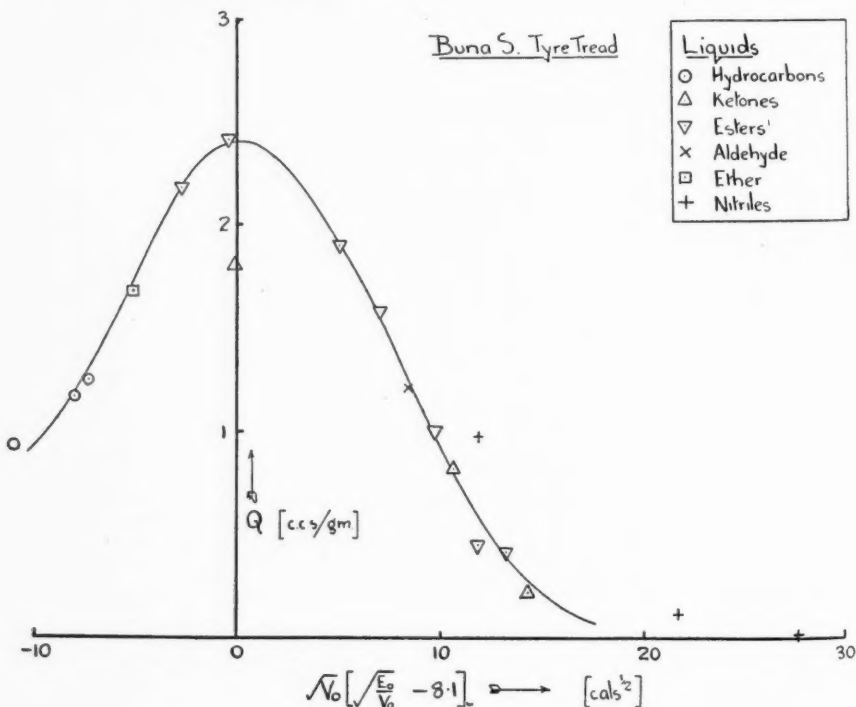


FIG. 4.

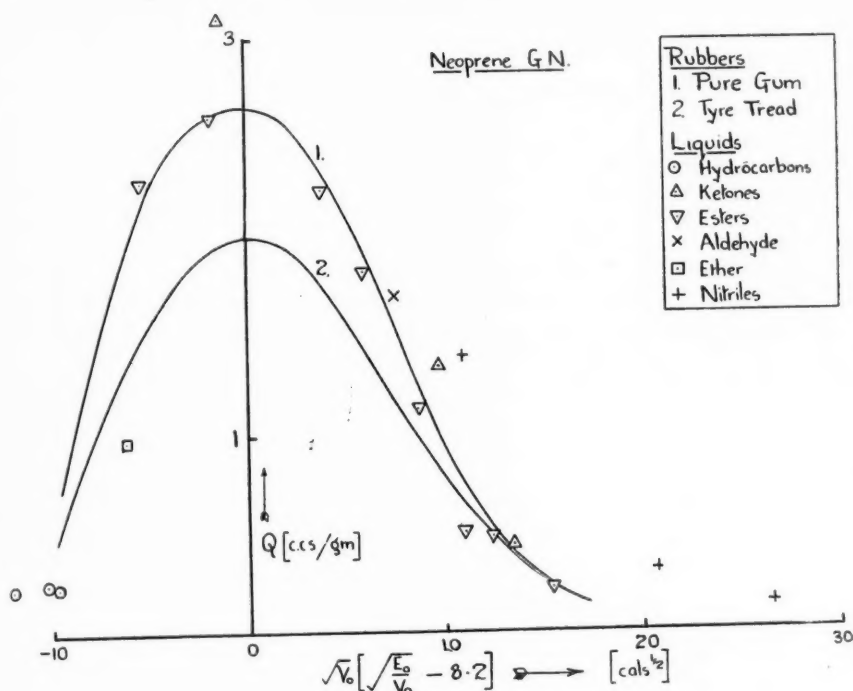


FIG. 5.

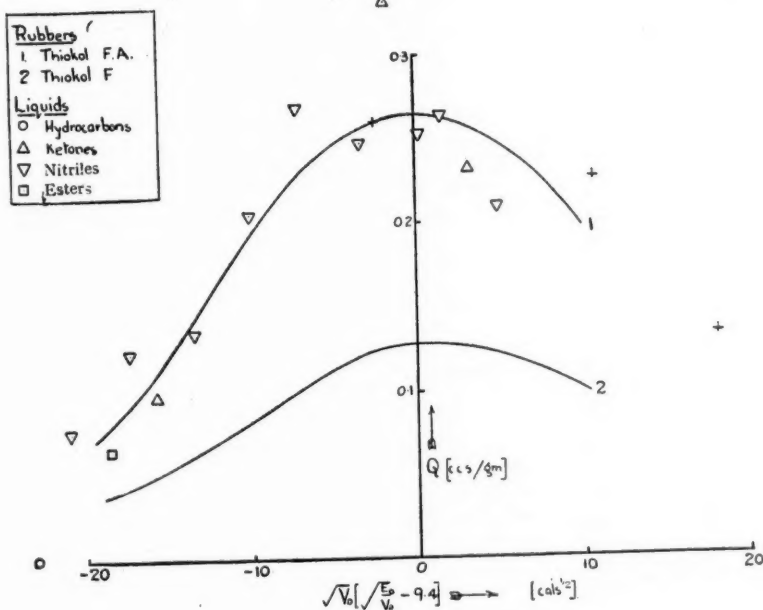


FIG. 6.

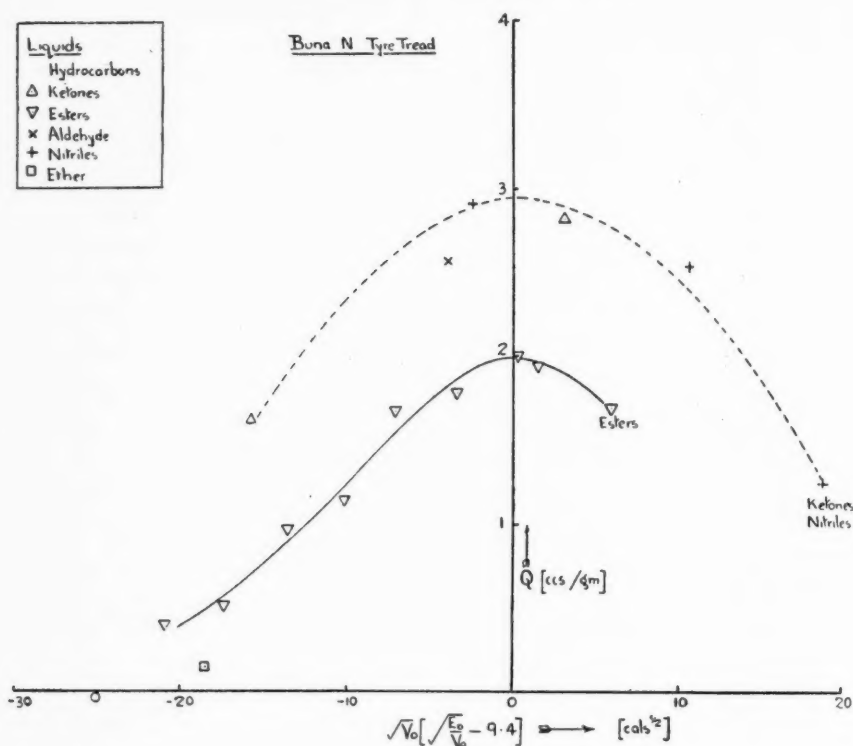


FIG. 7.

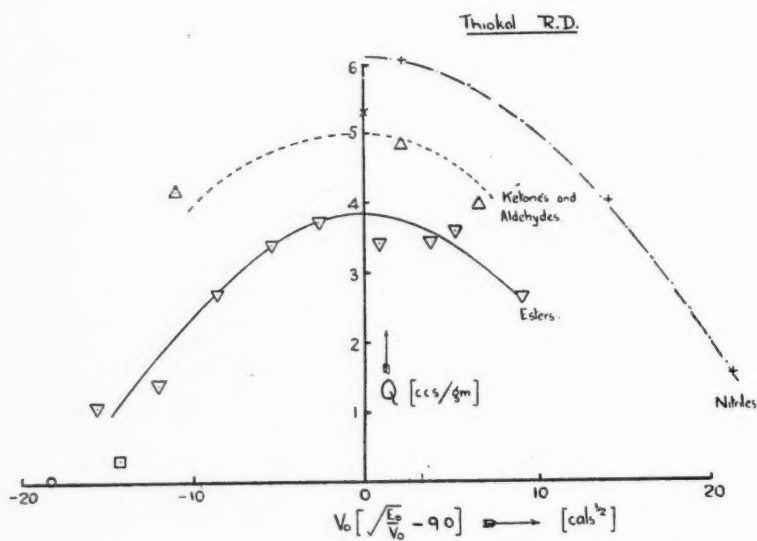


FIG. 8.

TABLE 4  
COHESIVE ENERGY DENSITIES OF RUBBERS

	Numbers	Cal. per cc.
Natural	1 to 5	63.7
Buna-S	13	65.5
Neoprene-GN	6 and 7	67
Thiokol-RD	10	81
Thiokol-F	9	88
Thiokol-FA	11	88
Buna-N	12	88

TABLE 5  
RUBBER COMPOUNDS USED

	Rubber No. (cf. Table 4)						
	6	7	9	10	11	12	13
Rubber (synthetic)	100	100	100	100	100	100	100
Diorthotolylguanidine	0.5	1	...	...	...	...	...
Magnesium oxide	4	10	...	...	...	...	...
Carbon black	...	35	60	60	60	50	55
Whiting	...	100	...	...	...	...	...
Nonox-S	2	2	...	...	...	...	...
Stearic acid	0.25	0.25	0.5	1	0.5	1	1
Zinc oxide	1	5	10	5	10	5	5
Diphenylguanidine	...	...	0.1	...	0.1	...	...
Dibenzothiazyl disulfide	...	...	0.35	1	0.35	1	1
Dibutyl phthalate	...	...	...	20	...	40	...
Agerite powder	...	...	...	1	...	...	...
Sulfur	...	...	...	1.5	...	2	2
Tar	...	...	...	...	...	...	5
Total	107.8	253.3	171	189.5	171	199	169
Time of vulcanization (min.)	30	30	50	15	50	45	45
Steam pressure (lb. per sq. in.)	40	40	50	30	50	40	40

TABLE 6  
SWELLING DATA

Liquid	Q in rubber No. (c.c.s. liquid/g actual rubber)						
	6	7	9	10	11	12*	13
n-Pentane	0.23	0.21	.000	.014	.002	-.04	0.93
n-Hexane	0.26	0.24	.000	.023	.005	-.03	1.17
n-Heptane	0.24	0.22	.000	.009	.002	-.05	1.25
Ethyl ether	0.98	0.82	.066	0.33	.076	-.15	1.68
Isobutyl n-butyrate	2.27	1.94	.034	1.10	.077	.40	2.18
n-Butyl n-butyrate	2.60	2.25	.052	1.41	.124	.52	2.42
n-Butyl acetate	2.23	1.58	.089	3.42	.206	1.15	1.90
n-Propyl acetate	1.82	1.31	.110	3.72	.269	1.68	1.58
Ethyl acetate	1.14	0.92	.121	3.43	.248	1.79	1.00
Ethyl formate	0.51	0.48	.122	3.45	.255	2.00	0.45
Methyl acetate	0.49	0.45	.127	3.60	.264	1.94	.42
Methyl formate	0.23	0.28	.103	2.65	.210	1.69	...
Diisopropyl ketone	3.1	1.71	.054	4.17	.098	1.63	1.81
Ethylmethyl ketone	1.35	1.05	.177	4.82	.332	3.43	.82
Acetone	0.45	0.39	.122	3.97	.232	2.82	.22
Butyraldehyde	1.70	1.25	.281	5.29	.590	2.47	1.21
n-Capronitrile	1.40	0.93	.107	6.04	.261	2.91	.97
Propionitrile	0.32	0.31	.113	4.00	.227	2.53	.11
Acetonitrile	0.14	0.11	.067	1.51	.135	1.24	.02

\* The negative values recorded are of course due to a loss of plasticizer.



The agreement between theory and experiment found for the synthetic rubbers is far worse than for natural rubber. Especially is this true of Thiokol-RD (Figure 8), for which each class of liquid falls on a separate curve. This discrepancy is not to be considered remarkable, as Equation (3) can be true only if there are no specific interactions between the two components of the mixture. When both rubber and swelling agents possess polar groups, such interactions must be general, and will lead to deviations from the simple theory. Other points for which the present theory affords no explanation are: the greater swelling power of aromatic liquids compared with aliphatic; and the small swelling of Thiokol-A, Thiokol-F, and Thiokol-FA in liquids covering a wide range of C.E.D. values (see Figure 6; Thiokol-A showed no measurable swelling in any of the 20 liquids used).

The purpose of the present paper is to point out the main factors governing the absorption of liquids by rubber and to show how the swelling of a given rubber in a given liquid may be roughly predicted. A complete quantitative theory must await much more extensive experimental work than is yet available. Certain conclusions of practical importance, however, emerge: first a rubber cannot be made oil-resisting by physical compounding; and, secondly, the chemical structures likely to give oil-resisting rubbers can be predicted with some confidence.

#### APPENDIX 1

##### ESTIMATION OF C.E.D. OF RUBBER FROM SWELLING DATA

According to the theory, the swelling  $Q$  is a function of  $\sqrt{V_0} \left( \sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_r}{V_r}} \right)$  which we may denote by  $x$ .  $Q$  has its maximum value  $Q_{\max}$  when  $\sqrt{\frac{E_0}{V_0}} = \sqrt{\frac{E_r}{V_r}}$  or  $x = 0$ . The  $Q \sim x$  curve is roughly of the form of the error function, so that we may write:

$$Q = Q_{\max} e^{-\beta x^2} \quad (4)$$

where  $\beta$  will in general not be a constant (as in the error function) but will be a function of  $x$ . This may be re-arranged to:

$$x = \pm \sqrt{\frac{1}{\beta} \log_e \frac{Q_{\max}}{Q}}$$

Substituting for  $x$ , gives finally:

$$\sqrt{\frac{E_0}{V_0}} = \sqrt{\frac{E_r}{V_r}} \pm \sqrt{\frac{1}{\beta V_0} \log_e \frac{Q_{\max}}{Q}} \quad (5)$$

Hence if  $Q_{\max}$  is estimated by a rough plot of  $Q$  against  $\sqrt{E_0/V_0}$  and  $\sqrt{E_r/V_r}$  plotted as a function of  $\sqrt{\frac{1}{\beta} \log_e \frac{Q_{\max}}{Q}}$ , the resulting curve will have a slope  $\sqrt{\frac{1}{\beta}}$  and an intercept of  $\sqrt{\frac{E_r}{V_r}}$ . This procedure is illustrated by Figure 9, drawn from the data for rubber mix 1 of Table 2 (the pure-gum mix of natural rubber).

## APPENDIX 2

## LIQUIDS USED FOR SWELLING MEASUREMENTS

In selecting the series of liquids to be used in the present work, choice was restricted to aliphatic liquids of a reasonably normal type, *e.g.*, highly associated liquids were excluded. Calculation of the C.E.D. of a liquid at room

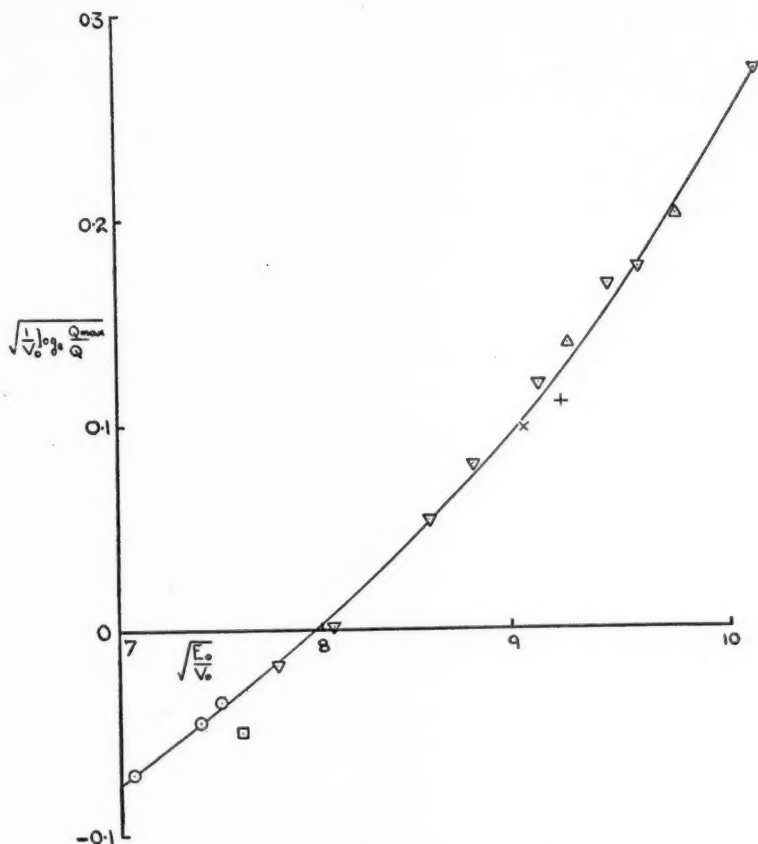


FIG. 9.

temperature requires an accurate knowledge of its latent heat of evaporation at room temperature. Where data were available, the molar latent heat  $L$  was calculated directly from the temperature coefficient of vapor pressure at 20° C, by means of the equation:

$$L = -R \frac{d \ln p}{d 1/T} \quad (6)$$

This equation is valid only provided the vapor behaves as a perfect gas; the correction for nonideality becomes significant if the vapor pressure exceeds 100 mm. Few data are available for the  $P.V.$  relationship of unsaturated

vapors, and the following method of correction was therefore employed. Cope, Lewis and Weber<sup>7</sup> showed that, if  $P_c$  and  $T_c$  are the critical pressure and temperature of a hydrocarbon, the departure of the vapor from the gas laws is a function of  $\frac{P}{P_c} \cdot \frac{T_c}{T}$ . Writing  $PV = \mu RT$ , these authors obtained a single curve of  $\mu$  against  $\frac{P}{P_c} \cdot \frac{T_c}{T}$  which represented all their data satisfactorily. In the present work, the same curve has been assumed to apply to all the liquids used. This assumption is doubtless not accurate, but suffices in view of the relatively small corrections involved. The corrected molar latent heat is given by  $L' = \mu L$ , where  $L$  is given by the Equation (6), and  $\mu$  was never less than 0.98.

In many cases,  $L'$  could not be obtained directly at 20° C, and it was necessary to calculate it from the value  $L_t$  at some other temperature  $t$ . If  $t - 20$  is not too large, the relationship is:

$$L' = L'_t \{1 - \Delta C_p(t - 20)\}$$

where  $\Delta C_p$  is the difference of molar specific heats between liquid and vapor. In the absence of precise data, a value of -10 calories per degree was used for  $\Delta C_p$ . Finally, the cohesive energy  $E_0$  is given by  $L' - RT = L' - 583$  calories per mole, so that:

$$E_0 = \mu L_t \{1 + 10(t - 20)\} - 583 \quad (7)$$

The liquids used, together with the values for  $E_0$ ,  $V_0$  and  $\sqrt{\frac{E_0}{V_0}}$  are listed in Table 7.

TABLE 7

	$E_0$ (cals. per mole)	$V_0$ (cc. per mole)	$\sqrt{\frac{E_0}{V_0}}$ (cals. per cc.) <sup>1/2</sup>
<i>n</i> -Pentane	5750	115.2	7.07
<i>n</i> -Hexane	7130	130.3	7.40
<i>n</i> -Heptane	8240	146.4	7.50
Ethyl ether	6000	103.8	7.60
*Isobutyl <i>n</i> -butyrate	10080	166.4	7.78
* <i>n</i> -Butyl <i>n</i> -butyrate	10750	165.7	8.06
<i>n</i> -Butyl acetate	9560	131.7	8.53
<i>n</i> -Propyl acetate	8810	115.1	8.75
Ethyl acetate	8060	97.8	9.08
Ethyl formate	7110	80.0	9.43
Methyl acetate	7310	79.7	9.58
Methyl formate	6360	61.6	10.16
Diisopropyl ketone	9250	141.7	8.08
Ethylmethyl ketone	7600	89.5	9.22
Acetone	7000	73.3	9.77
Butyraldehyde	7600	88.3	9.00
<i>n</i> -Capronitrile	10120	119.9	9.19
Propionitrile	8000	70.2	10.68
Acetonitrile	7420	52.5	11.89

\* Estimated from values for other esters, as no suitable vapor pressure data were available.

The work described in this paper forms part of the program of fundamental research undertaken by the Board of the British Rubber Producers' Association.

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# HOW SULFUR IS COMBINED IN VULCANIZED RUBBER\*

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## INTRODUCTION

Little is known with any degree of certainty about the way in which sulfur combines with rubber during vulcanization. It is the aim of the present work to examine, with the aid of Stuart molecular models, the various chemical reactions which have been suggested to explain the mechanism of vulcanization, and to decide which of these reactions may actually take place.

## THE MECHANISM OF THE REACTION BETWEEN RUBBER AND SULFUR

Fundamentally, two general types of combination of rubber with sulfur are possible<sup>1</sup>:

- (1) the formation of intermolecular sulfur bridges between chains of rubber molecules, with resulting formation of a network structure.
- (2) an intramolecular combination of sulfur with the individual chain molecules of rubber.

In addition, another mechanism of vulcanization is conceivable, whereby sulfur itself does not combine with rubber, but either the sulfur or accelerator promotes cyclization or polymerization of the rubber chains. Figure 1 shows, for example, three possibilities, any of which lead to intermolecular sulfur-free network structures.

Reaction (1) in Figure 1 is mentioned frequently in the literature, *e.g.*, it represents the polymerization of a compound such as cinnamic acid under the catalytic influence of ultraviolet radiation. In the case of rubber, this possibility should probably not even be considered, since a cyclization process of this character in unsaturated hydrocarbons has never been described.

On the contrary, reaction (2) in Figure 1, or some variation of this reaction, whereby there is a transfer of hydrogen and the formation of a single cross-linked compound, is in complete accord with the behavior of unsaturated hydrocarbons during polymerization<sup>2</sup>. On a basis of kinetics, the trimolecular reaction (3) in Figure 1 is very improbable.

In the case of certain polybutadienes, *e.g.*, polychloroprene (Neoprene), it is generally assumed that a polymerization reaction<sup>3</sup> takes place, as can probably be best represented by reaction (2) in Figure 1. The possibility that polymerization reactions of this character take place to any great extent in the case of rubber should not, however, be taken very seriously, for experiments have shown that the loss of unsaturation<sup>4</sup> and the changes in specific gravity and in refraction<sup>5</sup> as a result of vulcanization are proportional to the percentage of combined sulfur.

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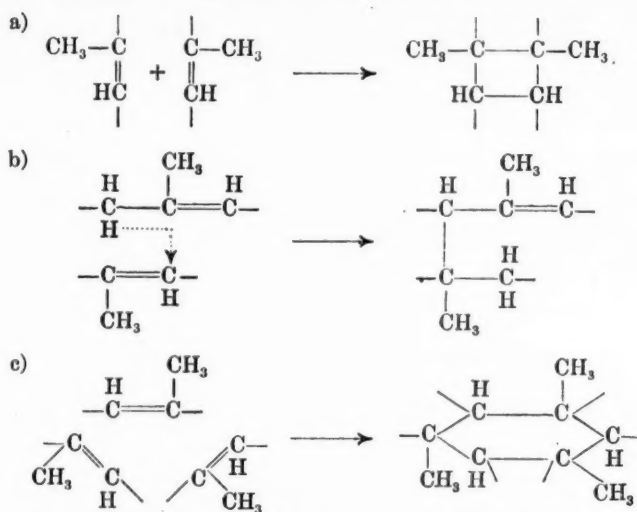


FIG. 1.—Possible polymerization reactions in the vulcanization of rubber, without combination of sulfur.

These polymerization reactions will not be discussed further in the present paper, since the object of the latter is only a study of the ways in which sulfur may combine with rubber. That, in any case, double bonds play a leading part in vulcanization is evident from the incapacity of hydrogenated rubber<sup>6</sup> and of polyisobutylene (Oppanol, Vistanex) to vulcanize. Nor will any special attention be paid to the question whether sulfur combines intermolecularly or intramolecularly, since this question involves many colloid-chemical problems. However, it is hoped to return to this subject later.

#### THE USE OF MOLECULAR MODELS

Among the various types of molecular models which have been found to be of service, those of Stuart<sup>7</sup> are best adapted to general use, because, with these models, the space filled by the atoms is represented in a particularly successful way. When atoms have united to form a molecule, the interatomic distance<sup>8</sup> in the direction of union is approximately 1–2 Å.U., while the interatomic distance between two molecules is approximately 2–4 Å.U. In atomic segment models of Stuart, which are shown in Figure 2 for aliphatic carbon, aromatic

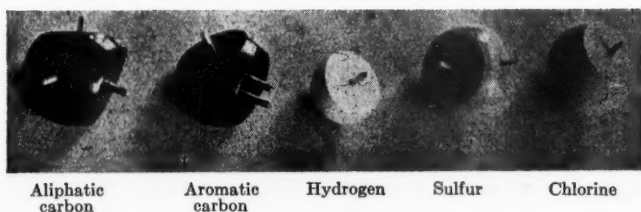


FIG. 2

carbon, hydrogen, sulfur and chlorine, this configuration is represented as a flattening, in which case the extension in the principal direction of linking is smaller than in the other directions.

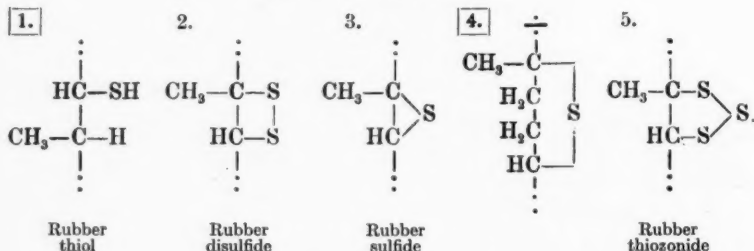


These atomic models are of particularly great help when it is desired to determine, on a basis of steric considerations, to what extent combination of atoms is possible, and when it is intended to study isomerization phenomena and the possibilities of free rotation<sup>9</sup>.

#### CLOSER EXAMINATION OF THE CHARACTER OF THE BOND BETWEEN SULFUR AND RUBBER

Rather than enter into a detailed discussion of the various theories which have been proposed, some theories in the literature which seem of particular importance<sup>10</sup> are combined in schematic form in Figure 3.

##### A. Intramolecular Bonding



##### B. Intermolecular Bonding

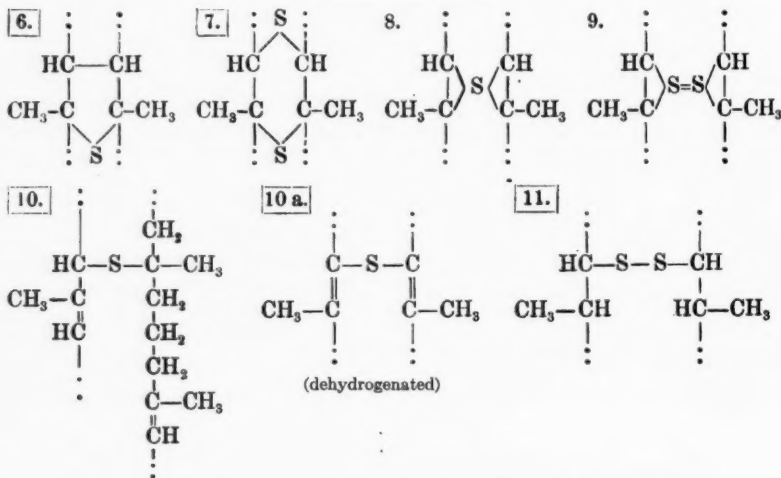


FIG. 3.—Types of combination of rubber with sulfur, drawn from the literature. Only the schemes with numbers in squares are possible of existence.

Differences other than those shown in Figure 3 are possible if sulfur is assumed to unite at other positions and, when necessary to the theory, when dehydrogenation takes place, as may be seen by comparing Scheme 10a with Scheme 10. It is on the basis of such a dehydrogenating action of sulfur that Fisher<sup>11</sup> based his theory of vulcanization. However, in this case it is necessary to assume that the hydrogen sulfide which is formed adds in turn more or less completely to the double bonds, because only traces of hydrogen sulfide can be detected during vulcanization, and a permanent state of dehydrogenation is consequently not even to be considered.

Dehydrogenation of the character described above is out of the question also because of earlier work in which it was proved that, in the final analysis, combination of each atom of sulfur is accompanied by the disappearance of one double bond. Such a phenomenon is to be expected only when there is no permanent dehydrogenation.

When it is attempted to construct, by means of Stuart models, the compounds shown in Figure 3-A, it is immediately evident that compounds in which sulfur is present in a 3-atom ring or in a 4-atom ring (Nos. 2 and 3) cannot be constructed from atomic models having normal valence angles. The deviations of these valence angles from the normal to form rings of this character are large, as is evident from Figure 4 and Figure 5, which illustrate

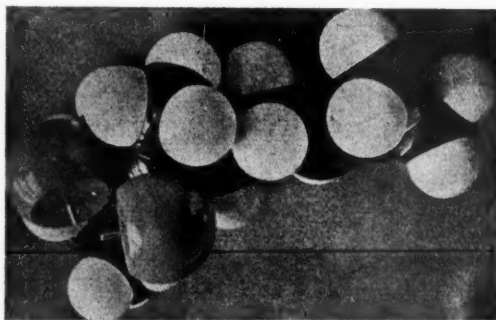


FIG. 4.—Compound No. 2. Rubber disulfide with four-atom ring.

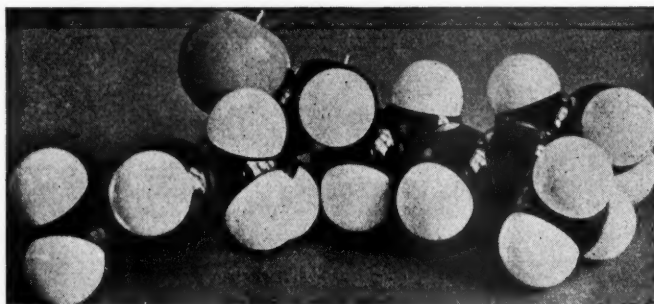
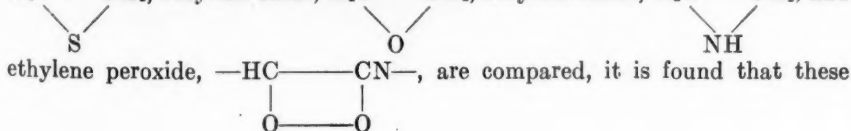


FIG. 5.—Compound No. 3. Rubber sulfide with three-atom ring.

compounds nos. 2 and 3. Such a large distortion of the valence angles in a molecule would lead to considerable internal stress and, in turn, would result in diminished stability.

It is wholly inconceivable, therefore, why among the many possible forms of combination, sulfur should show a preference for the less stable form. If similarly constituted compounds, such as derivatives of ethylene sulfide,  $\text{H}_2\text{C}-\text{CH}_2$ , ethylene oxide,  $\text{H}_2\text{C}-\text{CH}_2$ , ethylene imine,  $\text{H}_2\text{C}-\text{CH}_2$ , and



derivatives are in some cases difficult to prepare and that they react very easily; so much so, in fact, that some are even explosive.

For this reason, compounds like nos. 2 and 3 should be expected at best to be merely intermediate products of brief existence, which, at the temperatures of vulcanization, *e.g.*, 125° C, decompose rapidly in further reactions.

It is conceivable that compound no. 5 can exist as such<sup>12</sup> and, by means of a Stuart model, can be easily constructed. Yet this type of compound is quite improbable too, because the existence of such a configuration is wholly hypothetical and has never been demonstrated experimentally<sup>13</sup>.

Of the intermolecular compounds, nos. 6, 7, 10 and 11 can be constructed simply and directly with Stuart models, as illustrated in Figures 6, 7 and 8.

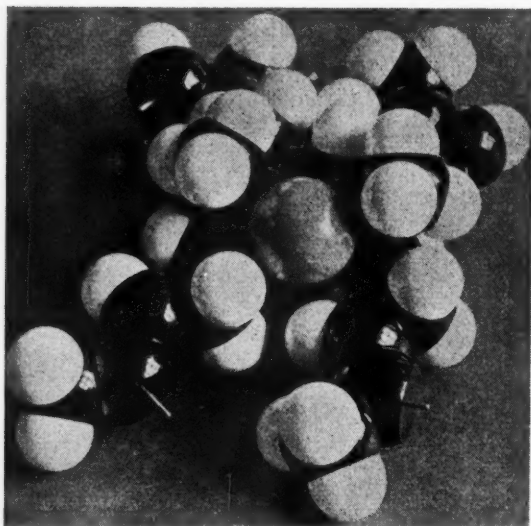


FIG. 6.—Compound No. 6. Model of intermolecular linking.

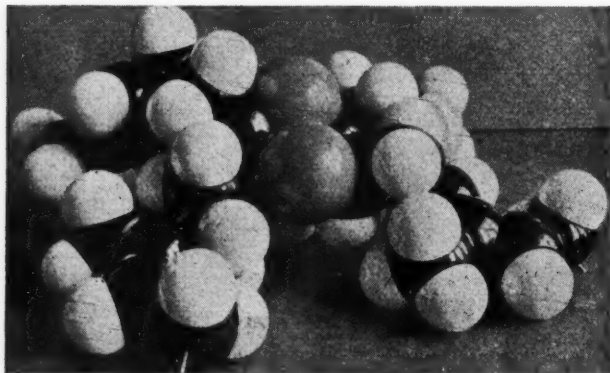


FIG. 7.—Compound No. 7. Model of intermolecular linking.



FIG. 8.—Compound No. 8. Model of intermolecular linking.

The remarks which apply to compound no. 3 apply also to compounds nos. 8 and 9, since these two have improbable configurations, with three-atom rings. It might be added that, in the case of compound no. 8, a configuration in which sulfur is combined in such a spiral fashion would in itself be extremely unusual.

In brief, then, it seems that, of the intramolecular compounds, only compounds nos. 1 and 4, and of the intermolecular compounds, only compounds nos. 6, 7, 10 and 11, are at all likely to be formed.

In view of the known reaction of cyclohexene with sulfur<sup>14</sup>, it is quite conceivable that thiol derivatives of rubber may be formed, at least as intermediate products. But it is improbable that thiol groups are present at the end of the reaction, because it is characteristic of these groups to react easily, with possible formation of a sulfide or a disulfide. In accord with this view is the fact that Hauser and Brown<sup>15</sup> could not detect thiol groups in vulcanized rubber. In the opinion of the present authors, therefore, sulfur would, in the case of intramolecular compounds, be combined chiefly in the form shown in compound no. 4. This is a type of compound which was first suggested by Midgley and his collaborators<sup>16</sup> as a result of experiments on the pyrolysis of ebonite, whereby thiophene derivatives were found.

Of the intermolecular compounds, represented by compounds nos. 6, 7, 10 and 11, it cannot for the moment be said with any degree of certainty which compounds may exist. Particular note should, however, be made of compound no. 10, which may be formed in a completely analogous way to the formation of compound no. 4 through the medium of the thiol compound (see Figure 9).

Suppose it be assumed that a thiol compound is formed during vulcanization as an intermediate product, *e.g.*, by the addition of hydrogen sulfide<sup>11</sup>, as in the reaction of cyclohexene with sulfur. Now it is known that thiol compounds react easily with double bonds, with formation of addition compounds<sup>17</sup>; hence according as a thiol group reacts with a double bond of its own molecule or with a double bond of a neighboring molecule, an intramolecular or an intermolecular sulfur bridge may be formed, as shown in Figure 9.

On this assumption, the types of reactions involved in the formation of intramolecular and intermolecular compounds differ from one another only in

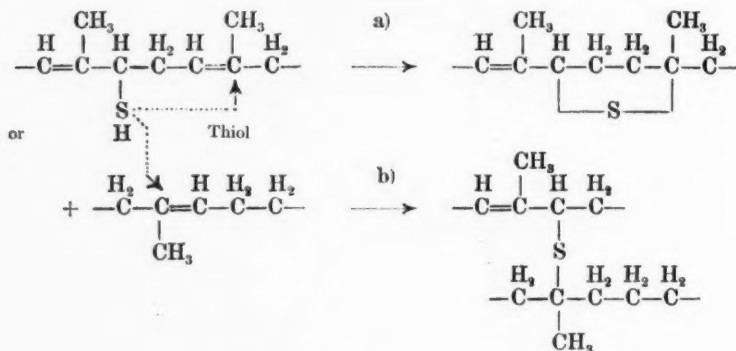


FIG. 9.—Scheme of possible reactions in the vulcanization process.

certain details. Final judgment as to the nature of the reactions which take place during vulcanization is, however, possible only after more extensive experimentation, in which it must be proved in what way sulfur reacts with olefins under various conditions and what are the reaction products which are formed in the decomposition of vulcanized rubber by ozone.

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# THE CHANGE IN THE RAMAN SPECTRA OF CHLOROPRENE AND ISOPRENE IN THE POLYMERIZATION PROCESS\*

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## INTRODUCTION

The structure of chloroprene and its polymers has been studied by Perumova<sup>1</sup> and Kubota<sup>2</sup> with the aid of Raman spectroscopy. However, the data obtained by these authors are rather contradictory. It follows from the work of Perumova that the Raman spectrum of chloroprene practically does not change in the polymerization process. The most significant shift is that of the frequency of the C=C bond from 1620 to 1626 cm.<sup>-1</sup>. Moreover, an increase in the intensity of the background in spectrograms was noted during polymerization.

The author suggests the hypothesis that this continuous background is due to the molecules of the polymers formed.

Kubota's data differ substantially from the results above. Kubota established that in the polymerization process, when chloroprene changes from liquid to solid, the intensity of the C=C frequency of the monomer (1628 cm.<sup>-1</sup>) decreases somewhat. A new frequency of a definitely smaller intensity appears (approximately equal to 1658 cm.<sup>-1</sup>), corresponding to the C=C bond in the polymer. The author points out that the ratio of intensities of the frequencies 1628 and 1658 cm.<sup>-1</sup> is such that, in the solid state, at least in the first stage, the greater part of the chloroprene is not polymerized through the formation of ordinary bonds, but is bound by van der Waals' forces.

It was of interest to establish what is the actual change in the Raman spectrum of chloroprene during polymerization, and to investigate the Raman spectra of polymers free of the monomer. This was carried out in the present work. For the purpose of comparison, we also investigated the Raman spectra of isoprene (a monomer having no polar substituent) during polymerization, and the Raman spectra of solutions of isoprene polymers in benzene and carbon tetrachloride.

## EXPERIMENTAL PART

### PURIFICATION OF THE SUBSTANCES INVESTIGATED

**Chloroprene.**—Technical chloroprene was distilled in a current of nitrogen under a pressure of 290 mm. Further purification of the chloroprene, after it had been treated with fused calcium chloride, consisted in distilling it in a Podbilniak column<sup>3</sup>. The chloroprene obtained was distilled *in vacuo* and collected in the vessels for Raman spectrography; benzoyl peroxide, used as the initiator of polymerization, had been introduced beforehand into these vessels (the amount of benzoyl peroxide was approximately 0.5 per cent of the weight of distilled chloroprene). The polymerization of chloroprene in the absence of benzoyl peroxide, proceeding by the action of oxygen of the air

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contained in the sealed vessel, was also investigated. Polymerization was carried out at 40° C at room temperature.

*Isoprene*.—Isoprene was separated from trimethylethylene by treating the mixture with cuprous chloride; the latter forms complexes with isoprene, which are destroyed on heating<sup>4</sup>. Isoprene free of trimethylethylene was dried over calcium chloride and distilled in a current of nitrogen, using a Podbilniak column; it was then distilled *in vacuo* into the vessel for Raman spectrography, which contained benzoyl peroxide (1 per cent of the weight of isoprene distilled). The vessel was placed in a thermostat, where polymerization proceeded at 70° for several days.

#### INVESTIGATION OF THE SAMPLES

We obtained the Raman spectra of the solutions of chloroprene and isoprene polymers in corresponding monomers at different stages of polymerization. After obtaining the Raman spectrum, the percentage polymerization was determined for the sample by evacuating the monomer in high vacuum.

We established that, on formation of highly polymeric molecules, there is no increase in the intensity of the continuous background in a spectrogram. However, as polymerization proceeds because of contraction of the polymerizing mass, bubbles appear in solid specimens, and these bubbles cause an increase

TABLE 1  
RAMAN SPECTRA OF CHLOROPRENE AND ITS POLYMERS

Chloroprene			A 30% solution of chloroprene polymers in the monomer $\nu$ cm. <sup>-1</sup> I	A solution of chloroprene polymers in a solvent $\nu$ cm. <sup>-1</sup> I	The chloro- prene polymer (100%) $\nu$ cm. <sup>-1</sup> I
Data from literature		Our data $\nu$ cm. <sup>-1</sup> I*			
Perumova $\nu$ cm. <sup>-1</sup> I	Tutomu Kubota $\nu$ cm. <sup>-1</sup> I				
3104	3113 (5b) e	3109 (2)	3108 (1½)	—	—
3070	—	—	—	—	—
3006	3015 (6) e	3018 (4)	3018 (4)	—	3025 (2)
2967	—	—	—	2951 (½)	2955 (1)
—	—	—	2913 (1½)	2910 (1½)	2915 (4)
—	—	—	2842 (1)	2845 (½)	2842 (1)
1620	1628 (15) e, k	1628 (10)	1657 (3), 1629 (10)	1657 (5)	1658 (10)
1574	1581 (4) e	1583 (2)	1585 (2)	—	—
1468	1526 (1) e	—	—	—	—
1411	1417 (6) e	1418 (5)	1437 (1), 1419 (5)	1432 (1)	1435 (4)
—	1381 (1) e	1383 (1)	1380 (1)	—	—
1334	1359 (0) e	1359 (1)	1358 (¾)	1341 (¾)	1340 (3)
1279	1287 (7) e	1286 (5)	1287 (5)	1281 (½)	1283 (2½)
1206	1214 (3) e	1215 (2)	1214 (2)	1220 (½)	1215 (1½)
—	—	—	1171 (¾)	1171 (¾)	1167 (1)
—	—	—	1111 (¾)	1113 (½)	1107 (1½)
1006	1020 (2) e	1018 (1)	1019 (1½)	1001 (¾)	1005 (5)
—	923 (2b) e	921 (1)	922 (2)	922 (½)	908 (¾)
—	882 (2b) e	880 (1)	886 (1)	—	—
722	735 (0) e	735 (0)	735 (0)	—	—
620	629 (6) e	630 (6)	630 (4)	587 (½)	587 (2)
514	518 (4) e	520 (3)	520 (3)	508 (½)	500 (1)
435	387 (3) e	388 (2)	384 (2)	—	—
(242)	249 (4b) e, 158 (1b) e	250 (1½)	249 (2)	—	260 (1)

\* The estimation of the intensities of Raman lines was based on the analysis of the microphotometer curves of the spectra, employing a 10-point scale.

in the intensity of reflected parasitic light and a corresponding increase in the intensity of the continuous background in spectrograms. We succeeded, however, in obtaining a spectrum of a 100 per cent polymer without any bubbles in its mass. It had the appearance of a compact, transparent rod. The contraction during polymerization proceeded in a manner such that a solid rod consisting of a polymer separated from the walls, forming an empty space between the walls of the vessel and the surface of the polymer (polymerization was carried out at room temperature). We did not observe any increase in the intensity of the continuous background in the Raman spectrum of the polymer itself.

Raman spectra of solutions of polymers in inert solvents (carbon tetrachloride and benzene) were also investigated. To obtain such a solution, the polymer was freed of the monomer by evacuation, using high vacuum.

The polymers reprecipitated by methanol as well as non-reprecipitated specimens were both studied. To obtain samples of polymers possessing greater solubility, chloroprene was polymerized with tetraline hydroperoxide in such a way that polymerization did not exceed 30 per cent.

The results are presented in Tables 1 and 2.

TABLE 2  
RAMAN SPECTRA OF ISOPRENE AND ITS POLYMERS

Isoprene			A 38% solution of isoprene polymers in the monomer $\nu$ cm. <sup>-1</sup> I	A 61% solution of isoprene polymers in the monomer $\nu$ cm. <sup>-1</sup> I	A solution of isoprene polymers in the inert solvent $\nu$ cm. <sup>-1</sup> I	The Raman spectrum of rubber <sup>5</sup> $\nu$ cm. <sup>-1</sup> I
Gehman and Osterhoff's data <sup>4</sup> $\nu$ cm. <sup>-1</sup> I	Dadiou and Kohlrausch's data <sup>6</sup> $\nu$ cm. <sup>-1</sup> I	Our data $\nu$ cm. <sup>-1</sup> I				
—	3083 (3)	3092 (2)	3089 (2)	3090 (2)	—	—
3012 (8)	3010 (5)	3012 (7)	3015 (6)	3011 (6)	—	—
2986 (2)	2083 (1)	2985 (1)	2986 (1)	2983 (1)	—	—
2930 (2)	2920 (2)	2931 (1½)	2932 (2)	2931 (2)	—	—
2908 (2)	—	2906 (2)	2910 (2)	2906 (2)	2917 (1½)	2915 (9)
2864 (1)	—	2860 (½)	—	2853 (1) dif	2851 (1)	—
—	—	—	1666 (3)	1665 (5)	1665 (5)	1670 (15)
1640 (15)	1636 (10)	1637 (15)	1636 (10)	1637 (10)	—	—
—	—	—	—	—	1542 (1)	—
1426 (8)	1420 (5)	1425 (6)	1422 (4)	1424 (5)	1430 (2)	1446 (7)
1388 (2)	1380 (1)	1385 (1)	1379 (1)	1383 (1)	1377 (1½)	1379 (7)
—	—	—	1330 (½)	1330 (½)	1327 (2)	1302 (1)
1296 (8)	1291 (5)	1290 (7)	1286 (5)	1290 (7)	1279 (2)	1220 (1)
—	—	—	—	1105 (¾)	1103 (1½)	1105 (1)
1070 (6)	1070 (4)	1067 (5)	1066 (4)	1066 (4)	1041 (1½)	1017 (1)
992 (3)	994 (2)	993 (2)	990 (1½)	992 (1½)	998 (2)	—
952 (6)	954 (4)	951 (4)	948 (3)	951 (3)	943 (0)	938 (1)
901 (5)	899 (3b)	903 (5)	904 (4)	904 (1½)	908 (0)	910 (1)
778 (3)	779 (2)	777 (3)	776 (1½)	776 (1½)	—	860 (1)
—	—	—	—	590 (0)	590 (0)	660 (1)
529 (6)	530 (4)	531 (4)	526 (4)	529 (4)	—	—
423 (3)	423 (2)	425 (2)	423 (1)	423 (2)	431 (1)	—
286 (2)	289 (1)	283 (1)	281 (½)	271 (1)	—	—

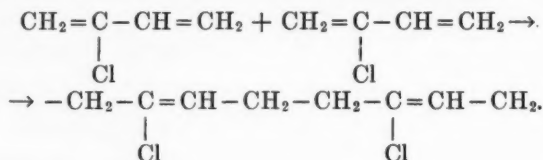
Let us note that when the Raman spectra of chloroprene polymers in an inert solvent were studied, the solutions employed were of a low concentration with respect to the polymer. Therefore, the data which characterize the frequencies of vibrations in a molecule of a chloroprene polymer obtained from the Raman spectrum of a pure polymer are more precise.

## RESULTS

The experimental results of the Raman spectra of chloroprene and isoprene are given in Tables 1 and 2.

Tables 1 and 2 show that, in the Raman spectra of solutions of chloroprene and isoprene polymers in the respective monomers, besides the C=C frequency, which characterizes a conjugate double bond in a monomer (1630 cm.<sup>-1</sup> for chloroprene and 1640 cm.<sup>-1</sup> for isoprene), there appears during polymerization a frequency (1660 and 1665 cm.<sup>-1</sup>, respectively), corresponding to an isolated double bond in a polymer.

The intensity of this frequency increases in the polymerization process, while the intensity of the frequency of the conjugate double bond corresponding to the monomer molecules decreases. However, in the specimens with a rather high polymer content (more than 50 per cent), the intensity of the frequency of the conjugate double bond is considerably greater than the intensity of the frequency of the isolated double bond (see Table 2). This is due to the fact that during polymerization a part of the double bonds disappears:



As follows from the results in Tables 1 and 2, to characterize the frequencies of vibrations in a polymer molecule, it is necessary to investigate its Raman spectrum in a medium containing no monomer. From the data obtained by the present authors (Table 1), it follows that, besides the shift of the frequency of the double bond from 1630 cm.<sup>-1</sup> to 1658 cm.<sup>-1</sup>, the Raman spectrum of the chloroprene polymer undergoes a number of essential changes. The splitting of the frequency of the double bond, which occurs in the spectrum of the chloroprene monomer, is absent in the case of the chloroprene polymer. New CH frequencies, 2955, 2915 and 2842 cm.<sup>-1</sup>, appear in the chloroprene polymer, while the frequency 3108 cm.<sup>-1</sup>, characteristic of unsaturated hydrocarbons, disappears. The CH deformation frequency,  $\delta_{\text{CH}}=1418$ , is shifted to 1435 cm.<sup>-1</sup>. A new intense frequency of 1340 cm.<sup>-1</sup> appears, instead of  $\delta_{\text{CH}}=1380$  cm.<sup>-1</sup> and 1359 cm.<sup>-1</sup>.

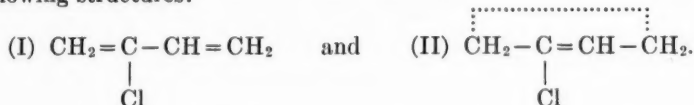
The frequency of the C—C valence vibration,  $\nu_{\text{C-C}}=1020$ , decreases to 1005 cm.<sup>-1</sup>, and its intensity increases considerably.

The frequency 630 cm.<sup>-1</sup> (which apparently corresponds to the C—Cl valence vibration) decreases to 537 cm.<sup>-1</sup>. The frequency of the deformation vibration of the carbon bond  $\delta_{\text{C-C}}=384$  cm.<sup>-1</sup> is not observed in the Raman spectrum of the chloroprene polymer. Furthermore, in the Raman spectrum of the polymer two new frequencies are observed, 1167 (1) and 1107 (1½). The frequency 1167 is apparently the deformation frequency of CH (the so-called outer deformation vibration, connected with the rotation of the CH group with respect to the C—C bond). The frequency 1107 lies in the region of the C—C valence vibrations (700–1100), and the outer deformation vibrations of CH (800–1200). Therefore, it can correspond to the C—C valence vibration as well as to the C—H deformation vibration, and also to their linear combination. On polymerization, the Raman spectrum of isoprene also undergoes a number of essential changes.

As is seen from Table 2, the Raman spectrum of the isoprene polymer is similar to that of rubber, as obtained by Gehman and Osterhoff<sup>9</sup>.

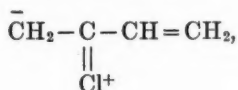
### DISCUSSION OF RESULTS

In the chloroprene and isoprene polymers, the frequency of the double bond is greater than the frequency of the conjugate double bond in the molecules of the corresponding monomers. The frequency of the double bond C=C is characteristic; therefore it is possible that the change observed here is related to the change in the character of the bond. A lower value of the frequency of the conjugate double bond compared with the isolated one is due perhaps to the fact that the chloroprene (and isoprene) molecules resonate between the following structures:



This explains the decrease in frequency of the double bond and the increase in frequency of the single bond.

Besides the two structures mentioned above, in the chloroprene molecule, on account of the polar substituent, there may exist the structure:



which also influences the frequency of the double bond.<sup>7</sup>

The presence of the resonance structure:  $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2$ , in butadiene is confirmed also by the data on interatomic distances, which are obtained from electron diffraction analysis. A considerable hindrance of free rotation around the C—C bond in butadiene is explained by the presence of the resonance structure.

On transition from polychloroprene to its monomer, one actually observes a lowering of the C=C frequency from 1658 cm.<sup>-1</sup> to 1628 cm.<sup>-1</sup>, and an increase in the C—C frequency from 1005 to 1020 cm.<sup>-1</sup>. The intensity of the frequency 1005 cm.<sup>-1</sup> in the polymer is considerably greater than in the monomer, because of the increase in the number of single bonds in the polymer.

In isoprene, on transition from polyisoprene to its monomer, one also observes the lowering of the frequency of the double bond from 1665 cm.<sup>-1</sup> to 1640 cm.<sup>-1</sup>. The frequency of the single bond, 1041 cm.<sup>-1</sup>, increases to 1067 cm.<sup>-1</sup>. The value of the frequency of the double bond in butadiene,<sup>8</sup> 1635 cm.<sup>-1</sup>, is close to the frequency of the double bond in the isoprene molecule—1637 cm.<sup>-1</sup>. Thus, the substitution of the CH<sub>3</sub> group in the butadiene molecule in position 2 does not affect the frequency of the double bond.

The appearance of new CH valence frequencies in the chloroprene polymer is due to the change in the structure of the chain on polymerization.

As follows from Table 3 (Nos. 4, 5, 6), the new CH frequencies, 2842, 2915, 2955 cm.<sup>-1</sup>, observed in the Raman spectrum of the chloroprene polymer are characteristic of the CH<sub>2</sub> group, bound to the carbon atom by a single bond. They are absent in those olefin and diene hydrocarbons in which the carbon

TABLE 3

Nos.	Hydrocarbon	Valence CH-frequencies				
1	Ethylene (liquid) <sup>9</sup>	—	—	—	3000 (5)	3080 (3)
2	Butadiene <sup>6</sup>	—	—	—	3000 (5)	3090 (2)
3	Chloroprene	—	—	—	3018 (4)	3109 (2)
4	Amylene <sup>10</sup>	2863 (5)	2936 (5)	2967 (2)	—	—
5	Piperylene <sup>6</sup>	2849 (2)	2916 (4)	2998 (4)	—	3089 (2)
6	Isoprene	—	2920 (2)	2983 (1)	3010 (5)	3083 (2)

atom of the  $\text{CH}_2$  group is bound to the neighboring C atom by a double bond (Nos. 1, 2, 3). On polymerization of chloroprene,  $\text{CH}_2$  groups, bound to the carbon atom by a single bond, actually appear, as we have already pointed out.

#### DISCUSSION OF THE DATA FROM LITERATURE

As already mentioned, Perumova, in investigating the Raman spectrum of chloroprene in the polymerization process, established that the only change in the spectrum by polymerization is the shift in the frequency from 1626 to 1620  $\text{cm}^{-1}$ .

It follows from our results that this conclusion is erroneous, and is probably attributable to the fact that the author studied samples with low polymer contents.

As follows from Table 1, our data on the Raman spectrum of chloroprene agree well with the data of Kubota and differ from the data of Perumova.

In the Raman spectrum of chloroprene, Perumova found a frequency of 435  $\text{cm}^{-1}$ . However, a sufficiently intense frequency of 24270  $\text{cm}^{-1}$ , corresponding to  $\Delta\nu_k = 435 \text{ cm}^{-1}$ , was also observed in the spectrum by the present authors. But one cannot refer it to 435— $k$ , since the corresponding satellite from the exciting line Hg  $e$  is absent. The frequency 24270  $\text{cm}^{-1}$  should be referred to 32023— $o$ , 3118— $q$ .

We did not observe the increase in the intensity of the continuous background, which, according to Perumova, is due to the highly polymeric molecules, either in the case of the samples with a high polymer content in the monomer, or in the 100 per cent polymer.

Kubota, in investigating the Raman spectra of solutions of chloroprene polymers in the monomer, observed the appearance of only one new frequency, 1658  $\text{cm}^{-1}$ .

However, as follows from our data, the Raman spectrum of chloroprene, besides the shift of the frequency of the double bond, undergoes a number of essential changes not reported by Kubota. This is due apparently to the fact that he studied solutions of low states of polymerization. This is proved by the ratio of intensities of the conjugate and isolated double bonds in the solution investigated by Kubota [1630(15), 1658  $\text{cm}^{-1}$  (3)]. Furthermore, the presence of the monomer makes it considerably more difficult to characterize the spectrum of the polymer.

In conclusion we wish to express our gratitude to M. W. Wolkenstein and J. K. Syrkin for their valuable advice.

#### SUMMARY

1. When chloroprene and isoprene polymerize, besides the frequency characterizing the conjugate double bond in the monomer, there appears a higher frequency corresponding to the isolated double bond in the polymer. In the

polymerization process, the intensity of the frequency of the conjugate double bond decreases and the intensity of the frequency of the isolated double bond increases. Because of the increase in the number of single bonds in the polymer, the intensity of the frequency of the single bond 1005 in the polymer is considerably greater than in the monomer.

2. Even in the case of the samples with high polymer contents (greater than 50 per cent), the intensity of the frequency of the conjugate double bond is considerably greater than the intensity of the frequency of the isolated double bond. This is attributable to the fact that part of double bonds disappear during polymerization.

3. The Raman spectra of the chloroprene and isoprene polymers differ essentially from those of the monomers. To characterize the frequencies of vibration in the polymer molecule, it is essential to investigate its Raman spectrum in a medium free of the monomer.

4. The formation of highly polymeric molecules on polymerization does not result in an increase in the intensity of the continuous background in spectrograms.

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# THE CRYSTAL STRUCTURE OF RUBBER HYDROCHLORIDE\*

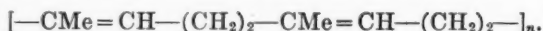
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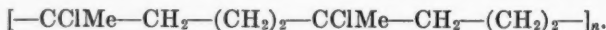
"Rubber hydrochloride", the crystalline substances made by addition of hydrogen chloride to rubber, is of interest for two reasons. First, the periodicity along the fibre axis of drawn specimens<sup>1</sup> indicates that the carbon chain has not the simple plane zigzag form found in paraffin hydrocarbons<sup>2</sup>, but is somewhat shortened by folding. There is similar evidence that several other chain polymers also have folded chains<sup>3</sup>; the elucidation of the geometry of such molecules would form a useful contribution to our knowledge of the stereochemistry of carbon compounds in general and chain polymers in particular. Rubber hydrochloride appeared to be a suitable substance for crystallographic investigation from this point of view: it gives a well-defined x-ray diffraction pattern. Moreover, a prediction of the chain form has been made on the basis of a knowledge of the periodicity and the use of a hypothesis which has been called the principle of staggered bonds<sup>4</sup>. The determination of the structure by x-ray methods forms the first test of the validity and usefulness of this hypothesis.

Secondly, rubber hydrochloride is interesting on account of its physical properties. Unlike rubber itself, it is crystalline at room temperature, "melting" at about 115° C. The present work on its crystal structure forms part of a program of research being carried out in this laboratory, and is a contribution to the attempt to understand the physical properties of chain polymers in terms of molecular structure.

*Chemical structure.*—The chemical structure of rubber is:



Hence, on the assumption that hydrogen chloride adds according to Markownikoff's rule, the chemical structure of rubber hydrochloride is expected to be:



*Experimental details.*—The crystal structure was deduced from x-ray diffraction photographs taken with copper radiation filtered through nickel foil to remove the  $K\beta$  wave-length. Two types of photograph were used—the usual fibre photograph, with the beam perpendicular to the fibre axis, and also photographs taken while the fibre axis was oscillating with respect to the beam. In both cases the spots were recorded on a cylindrical film, for the sake of obtaining the maximum angular range of reflections. The second type of photograph yielded reflections from planes perpendicular or nearly perpendicular to the fibre axis, some of which do not appear on the first type of photograph.

The best orientation of crystals in the specimens was obtained by drawing out a thin strip at 90°, and allowing it to cool while still extended. The normal fibre photograph shows 24 reflections, the intensities of which were estimated

\* Reprinted from the *Journal of the Chemical Society*, November 1942, pages 654–658.

visually. Attempts to obtain a double orientation by rolling strips of material failed; it was therefore not possible to obtain direct information on the orientation of crystal planes; interpretation rests simply on the positions of the spots on the photographs.

*Unit cell dimensions.*—The cell spacing along the fibre axis can be measured directly from the layer-line separation on the normal fibre photograph, and is found to be 8.95 Å.U. The cell dimensions in the directions perpendicular to the fibre axis cannot be measured directly, but all the spots on the photograph are found to fit a rectangular cell with  $a = 5.83$ ,  $b = 10.38$ ,  $c$  (fibre axis)  $= 8.95$  Å.U. From these dimensions, and the reported density of 1.193<sup>1</sup>, the number of  $-\text{CMeCl}-(\text{CH}_2)_3-$  units in the cell is found to be 3.8. There are evidently four of these units in the cell. On this basis, the true density of a single crystal is calculated to be 1.255. The lower density of the bulk material is presumably due to the presence of a certain amount of amorphous material, which, being inefficiently packed, would be expected to have a lower density than the crystals. Specimens of long-chain polymers usually have somewhat low densities for this reason. In the case of rubber hydrochloride, there is a second reason why the amorphous material is expected to have a low density; hydrochlorination in the specimens examined was not complete, the chlorine content being only 29.3 per cent (calculated for  $\text{C}_5\text{H}_7\text{Cl} : \text{Cl}$ , 34%), and unreacted molecules or sections of molecules, which would be lighter than the rest, are expected to form part of the amorphous material.

*Space group and parameters.*—The space-group symmetry of single crystals can usually be determined unambiguously by observing which types of x-ray reflection are systematically absent, and combining this information with that provided by crystal morphology and pyro- or piezoelectric properties. The problem is more difficult in the case of polymers, since these substances cannot be obtained in the form of single crystals; not only can no information be derived about crystal habit and pyroelectric properties, but frequently the information about absent reflections is ambiguous, owing to the overlapping of spectra. This means that usually a number of different space groups must be considered. To shorten the search for the correct arrangement, it is desirable to use external evidence, if this appears to limit the possibilities.

For rubber hydrochloride, it is found that, among reflections which can be uniquely indexed, the only systematic absences are the odd orders of  $0k0$ , and also  $h0l$  reflections having  $l$  odd; if these absences are not accidental, it appears that there is a screw axis parallel to  $b$ , perpendicular to which is a glide plane with translation  $c/2$ . Since the cell is rectangular, the symmetry would be expected to be orthorhombic; but there is no orthorhombic space group giving the particular combination of absences mentioned; in fact, the absences indicate the monoclinic space group  $P2_1/c$ . There remains, however, the doubt whether some of the "absent" reflections really have small intensities but are too weak to be detected on the photographs; in view of this doubt, it is necessary to consider the stereochemistry of the molecules themselves.

The chain form of rubber hydrochloride molecules has already been predicted<sup>4</sup> on the assumption that the bonds of singly-linked carbon atoms are staggered, the only chain form which has approximately the identity period found in rubber hydrochloride (8.95 Å.U.) is the form  $A_3BA_3C$  (Figure 1). This chain is also consistent with the probable chemical linking in the molecule (Markownikoff's rule being assumed); the section  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  would be likely to have the plane zigzag chain (an  $A$  sequence) as in polyethylene; only at the  $>\text{CMeCl}$  unit is there likely to be a  $B$  or  $C$  link. The chain

$A_3BA_3C$  has a glide plane with translation  $c/2$ , and the presence of methyl and chlorine substituents (provided they are in equivalent stereo-positions) does not affect this symmetry; the space group  $P2_1/c$  is thus consistent with the suggested chain form.

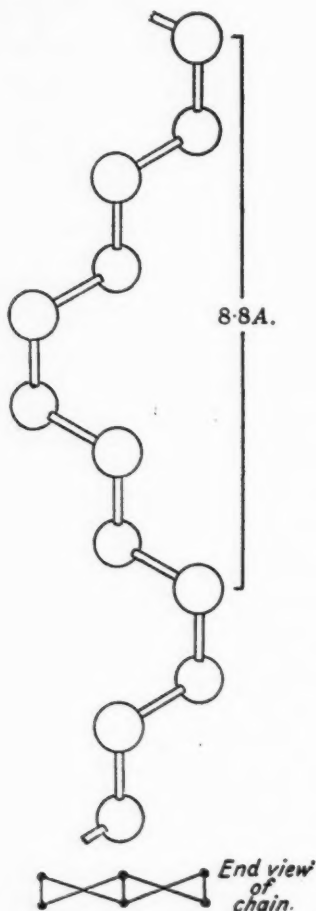


FIG. 1.—Chain type  $A_3BA_3C$ .

On the assumption, then, that this monoclinic space group and the suggested chain form are correct, it remains to determine the atomic parameters by calculation of the intensities of the reflections. Since in the identity period of the molecule there are two  $[-CMeCl-(CH_2)_5-]$  units, and the number of such units in the cell is four, there must be two chain molecules passing through the cell. The orientation of these molecules is fixed; the glide plane is perpendicular to the  $b$  axis. There are two alternative positions for the methyl and chlorine substituents; either the chlorine is on bond  $p$  (Figure 4), while the methyl is on bond  $q$ , or the reverse may be true. The decision that the

former is correct, as well as the relation of the chains to the screw axis and the precise atomic parameters, rest on calculations of the intensities of all the reflections. Satisfactory agreement between observed and calculated intensities is attained if it is assumed that the atoms occupy the positions given in Table I. The intensities are given in Table II. The predicted chain structure and the space group  $P2_1/c$  are evidently correct.

TABLE I  
ATOMIC PARAMETERS IN FRACTIONS OF UNIT CELL EDGES

	$x$	$y$	$z$		$x$	$y$	$z$
CH <sub>3</sub> (1)	0.204	0.238	0.032	CH <sub>3</sub>	0.281	0.51	0.32
CH <sub>2</sub> (2)	0.293	0.356	0.126	Cl	-0.11	0.39	0.283
C	0.195	0.371	0.285	CH <sub>2</sub> (3)	0.293	0.252	0.37

If the coördinates of any atom are  $x, y, z$ , there are corresponding atoms in the same chain at  $x, \frac{1}{2} - y, \frac{1}{2} + y$ , and in the second chain at  $x, \bar{y}, \bar{z}$  and  $x, \frac{1}{2} + y, \frac{1}{2} - z$ .

*Description of structure.*—Figures 2, 3, and 4 show projections on planes perpendicular to the three axes of the crystal. Figure 5 shows one repeating

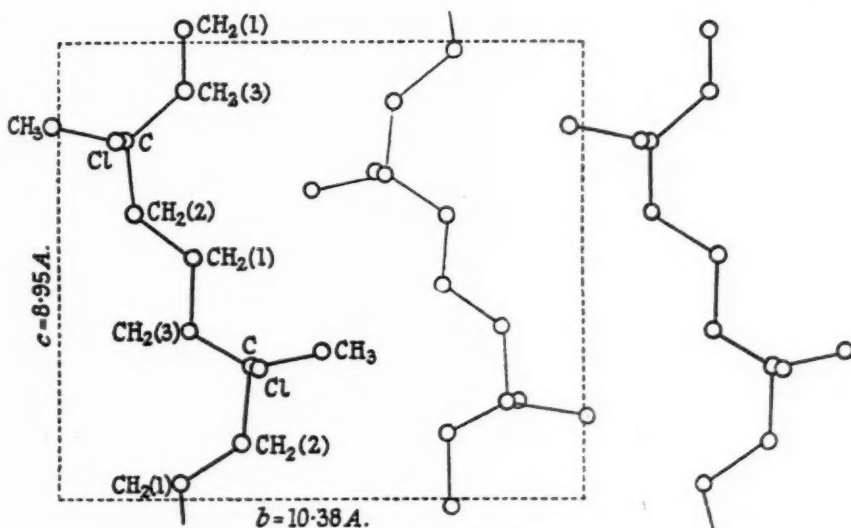


FIG. 2.—Crystal structure of rubber hydrochloride seen along the  $a$  axis.

unit of the rubber hydrochloride molecule. The predicted chain form is definitely confirmed. The results of this work thus demonstrate the usefulness of the principle of staggered bonds, on which the prediction was based, and also provide still another example in which the principle is obeyed.

No great accuracy can be claimed for the values of the atomic parameters on account of the small amount of information on which they are based. The possible errors of the parameters also vary with the diffracting power of the atoms concerned. By displacing the atoms by definite amounts and calculating

TABLE II  
COMPARISON OF OBSERVED AND CALCULATED INTENSITIES

Index	Intensity		Index	Intensity		Index	Intensity		Index	Intensity		Index	Intensity	
	Calcu- lated	Ob- served		Calcu- lated	Ob- served		Calcu- lated	Ob- served		Calcu- lated	Ob- served		Calcu- lated	Ob- served
010	0	0	320	0	0	051	0	0	212	34	vw	203	0	0
100	74	m	060			151			042	49	w	213		
020	231	vs	250	21	vvw	301	64	m	222			043	31	vvw
110			330			241			142	91	w	223		
120	0	0	160			311			232	18	0	143	2	0
030	0	0	011	14	0	321	8	0	052	0	0	233	0	0
130			101	0	0	060			152			053	0	0
200	190	s	021	338	vs	251	47	vvw	302	18	0	153		
210	34	m	111			331			242			303		vvw
040	14	0	121	107	m	012	20	0	312			243		
220			031	4	0	102			322	2	0	313		
140	34	w	131	10	0	022	176	s	103	0	0	*001	0	0
230	32	vw	201	48	w	112			023	82	vw	*002	157	s
050	0	0	211			122	5	0	113			*003	46	m
150			041	2	0	032	0	0	123	100	w	*013		
300			221	7	0	132	20	vw	033	1	0	*004	23	w
240	79	m	141						133	22	0	*104		
310			231	10	0	202								

\* The intensities of these planes were estimated independently from a photograph taken with the fibre axis horizontal and oscillated about a vertical axis between 45° and 90° to the x-ray beam.

No corrections have been made for thermal vibrations of the atoms. For this reason, the observed intensities should fall away from the calculated intensities with increasing angle of reflection. This does, in fact, occur.

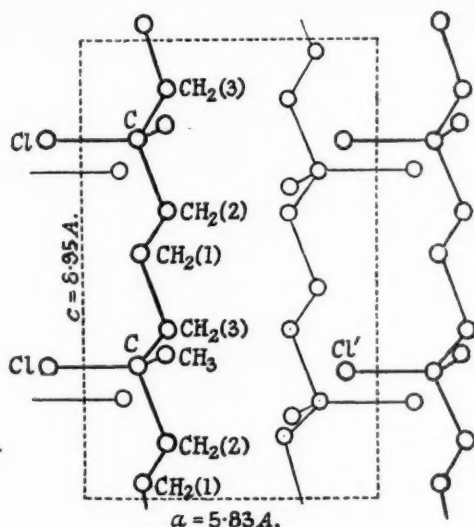


FIG. 3.—Crystal structure of rubber hydrochloride seen along the  $b$  axis.

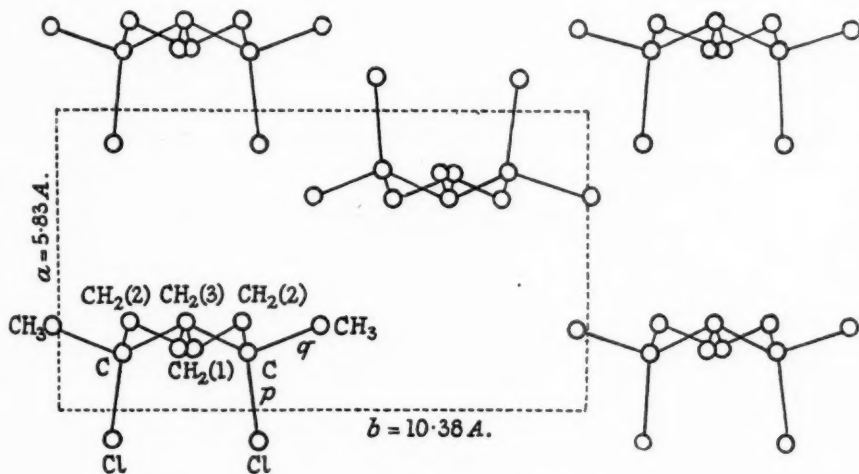


FIG. 4.—Crystal structure of rubber hydrochloride seen along the  $c$  axis.

the intensities, we assess the possible errors at about 0.02 Å.U. for chlorine and 0.05 Å.U. for carbon atoms.

Within the above limits of experimental error, all C—C distances have the normal value of 1.54 Å.U., and the C—Cl distance is 1.79 Å.U. (compare 1.77 Å.U. in polychloroprene). The nearest distances between carbon atoms in different chains vary from 3.89 Å.U. to 4.11 Å.U., and between carbon atoms and chlorine atoms in different chains from 3.76 to 3.83. None of the bond angles between carbon atoms in the chains differs by more than 4° from the



value of  $112^\circ$  found for a paraffin chain<sup>2</sup>. The angles made by the  $C-CH_3$  bond with the two adjacent  $C-CH_2$  bonds, however, deviate considerably from the normal value. The angle  $CH_2(3)-C-CH_3$  (Figure 6) is  $124^\circ$ , and the angle  $CH_2(2)-C-CH_3$  is  $100^\circ$ . The apparent reason for these abnormal angles is the repulsion of the  $CH_3$  group by  $CH_2(1)$ ; this has the effect of enlarging the angle  $CH_2(3)-C-CH_3$  and at the same time diminishing the angle  $CH_2(2)-C-CH_3$ . An exactly similar distortion of the methyl group from the "ideal" position has been found in rubber<sup>4</sup>, and this too can be attributed to the same cause.

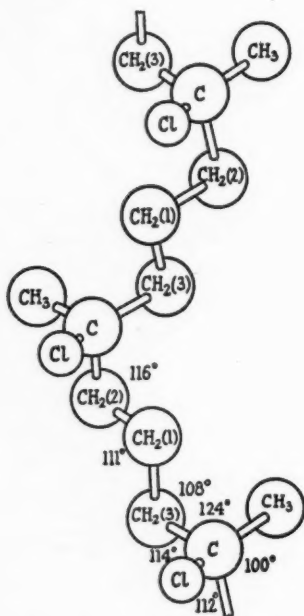
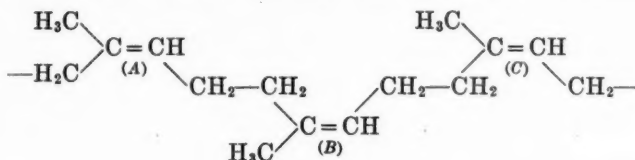


Fig. 5.—Geometry of the rubber hydrochloride molecule.

The mode of packing of the molecules shows clearly the reason why the angle  $\beta$  (which in the monoclinic system is not fixed by symmetry) is in this crystal  $90^\circ$ . The chlorine atom of one molecule ( $Cl'$  in Figure 3) fits into the hollow formed by groups  $CH_3$ ,  $CH_2(2)$ , and  $CH_2(3)$  attached to carbon atom C of the molecule in front, *i.e.*, the next molecule along the  $a$  axis. This packing ensures that the  $z$  coördinate of  $Cl'$  is about the same as that of C, and since the carbon-chlorine bond is at right angles to the chain axis, the angle  $\beta$  must necessarily be approximately  $90^\circ$ .

*Stereochemistry of the reaction between hydrogen chloride and rubber.*—In the first place, the structure of rubber hydrochloride now established confirms the original assumption that Markownikoff's rule is obeyed in the addition reaction; the chlorine atom adds on to the carbon bearing the methyl side group, and the hydrogen adds on to the  $=CH-$  group. But in addition, it is noteworthy that, in the rubber hydrochloride molecule, successive  $-CH_2)_3-CMeCl-$  groups are alternately left- and right-handed. (The enantiomorphic character of the group does not depend on the geometry of

the chain; it is not possible, by rotating round single bonds, to convert a left- into a right-handed unit.) The precise geometry of the addition reaction depends on the form of the rubber molecule in solution, *i.e.*, whether it is extended or coiled up. If it is extended in solution it may be represented thus:



Actually the molecule is not planar<sup>2</sup>, but the above plane projection is sufficient for the present purpose. The established structure of rubber hydrochloride implies that if a molecule of hydrogen chloride adds on to double bond A on this side of the rubber molecule—above the plane of the paper—then addition to B and C must also occur on this same side of the rubber molecule; and so on for many units, to give a molecule which is regular for at any rate some hundreds of A's (this being the order of size of the crystals of rubber hydrochloride). If the rubber molecules are coiled up in solution, the geometry of the addition reaction is different, but again some geometrically regular repetition must occur; in other words, it appears that when a hydrogen chloride molecule has added on to one double bond, the atomic grouping so formed has a directing influence on the process of addition to the next double bond.

It is interesting in this connection to note that balata hydrochloride is amorphous<sup>1</sup>. Balata or gutta-percha hydrocarbon is *trans*-polyisoprene; rubber is the *cis*-form. The amorphous character of balata hydrochloride may mean that, owing to the difference in chain structure, addition of hydrogen chloride does not occur in the geometrically regular way noted in the case of rubber, but in such a way that left- and right-handed groupings are formed indiscriminately, yielding chain molecules which since they are geometrically irregular in structure, cannot form crystalline arrangements.

*Physical properties of rubber hydrochloride.*—The mechanical properties of rubber hydrochloride are similar to those of other crystalline polymers: it can be drawn out to several times its length, the crystals becoming oriented in the process, and it remains extended when released. Near the m.p., the extensibility becomes reversible, the material then being more like rubber<sup>1</sup>. This behavior is typical also of crystalline polymers. Interest centers on the m.p., which is about 115°, *i.e.*, very much higher than that of rubber (about 0°) and similar to that of polyethylene (115°).

It has been suggested that ease of rotation round the single bonds of long-chain polymer molecules plays a large part in determining the m.p., and that the ease of rotation round the single bonds in any particular molecule is determined by two factors—the bond-orientation energy and the interaction of the atoms or groups held by the bonds. With respect to the second factor, we have to imagine, in the case of the rubber hydrochloride molecule, rotation occurring round bond C—CH<sub>2</sub>(2) in Figure 5, and to consider to what extent the rotation of CH<sub>2</sub>(1) is hindered by CH<sub>2</sub>(3), CH<sub>3</sub>, and Cl. [Rotation round bond C—CH<sub>2</sub>(3) presents the same geometrical problem.] The hindrance offered by CH<sub>2</sub>(3) or by the CH<sub>3</sub> group would be expected to be similar to the hindrance in rubber itself, since the configurations of the moving parts are

similar in the two molecules. The hindrance offered by the chlorine atom is expected to be less, since the chlorine atom is a little smaller than a  $\text{CH}_2$  or a  $\text{CH}_3$  group, and also stands further from the carbon atom to which it is attached. Thus, whatever bond rotations occur in the rubber hydrochloride molecule at the m.p., the geometrical hindrance to rotation is not likely to be greater, and may even be less, than in rubber itself. The high m.p. of rubber hydrochloride in comparison with rubber is, therefore, not to be explained by any steric effects.

Turning to the other factor—the bond-orientation energy—we find that rotation round single bonds is easier when there is an adjacent double bond (as in rubber) than in a saturated molecule<sup>4</sup>. The difference between the m.p.'s of rubber and of its hydrochloride may therefore be due, at any rate partly, to the fact that in rubber every fourth chain bond is a double bond, whereas the hydrochloride molecule is saturated, and the more rigid simply on that account. There are, however, other factors which may also play a part; first, the greater inertia of the moving parts of the rubber hydrochloride molecule, owing to the presence of the comparatively heavy chlorine atom, and, secondly, the interaction of C—Cl dipoles. Both these factors would tend to increase the m.p. It is not possible at present to assess the relative contributions of these factors.

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## PROPERTIES OF SOME SYNTHETIC RUBBERS\*

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### X-RAY STRUCTURE OF SYNTHETIC RUBBER

In presenting a series of x-ray diagrams of various types of synthetic rubber in comparison with natural rubber, in both the stretched and the unstretched condition, it is our purpose to bring out the fact that the molecular structure of synthetic rubbers is entirely different from that of natural rubber. It is proposed also to review briefly the theories which have been advanced, based on the x-ray analysis of rubber, to account for the elasticity of natural rubber, and to advance the possible reason for the difference shown by the x-ray diagrams of synthetic rubber.

At the present time, from the most general point of view, the molecular structure of a rubberlike material is envisaged as a sort of brush-heap structure of entangled long chain molecules<sup>1</sup>. x-Ray diffraction patterns show that, for some rubberlike materials, notable regularities of structure sometimes occur in the tangle of long-chain molecules. It is now realized that these regularities are not essential for rubberlike behavior. Nevertheless their observation and study is important because they afford a unique opportunity for studying the molecular structure of the chains and the molecular rearrangements which occur with the application of stress.

Under ordinary circumstances, the x-ray diffraction pattern of natural rubber consists of a broad halo similar to that obtained for liquids. This halo is shown in Figure 1. On stretching, sharp diffraction spots appear, as shown in Figure 2. This phenomenon was first observed by Katz<sup>2</sup>. Since then it

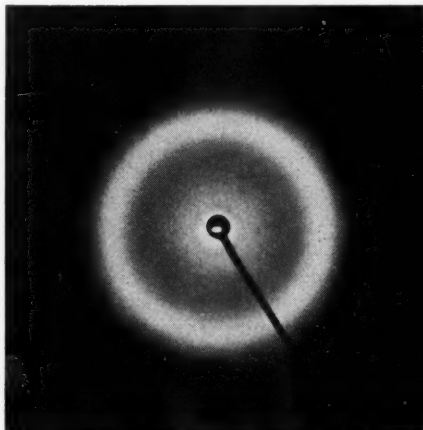


FIG. 1.—Rubber unstretched.

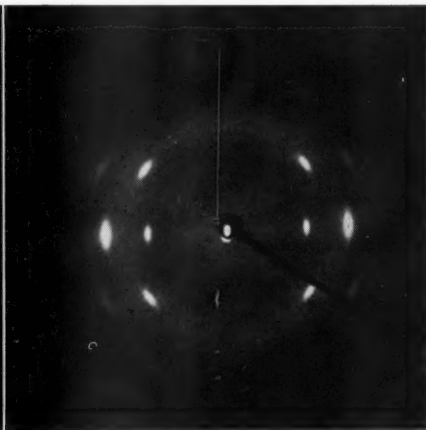


FIG. 2.—Rubber stretched.

\* Reprinted from the *India Rubber World*, Vol. 103, No. 6, pages 37-40, March 1941. This paper was presented at the annual meeting of the Society of Automotive Engineers, Detroit, Michigan, Jan. 6-10, 1941.

has been the subject of many investigations. For further details and the present status of the work, a review article may be consulted<sup>3</sup>.

A pattern such as that shown in Figure 2 indicates the presence of small, ordered crystalline regions. The crystallites are aligned in the direction of the stretching. The explanation of the appearance of these crystalline regions is somewhat involved in conjecture. What happens, apparently, is that, under the action of the applied stress, relatively short lengths of adjacent long-chain molecules are straightened and approximately aligned and positioned with respect to each other. As a result of these favorable circumstances, spontaneous crystallization can then occur, due to intermolecular forces which are sufficiently strong and regular to result in a crystal lattice. A single long-chain molecule is thought of as traversing a number of the ordered regions or crystallites<sup>4</sup>.

The alignment of the crystallites in the direction of stretching is somewhat analogous to the changes in structure which occur in the cold working of metals.<sup>5</sup> One of the fundamental differences lies in the fact that crystal grains exist in the metal before working and are brought into alignment by the working. In the case of rubber, the crystallites are not only aligned, but are brought into existence by stretching. The formation of crystallites in stretched rubber is responsible for some characteristic properties of rubber which are analogous to the strain hardening of metals. Thus, stiffening occurs at higher elongations, and the stress-strain curve is concave toward the stress axis. There is a reduction in creep or plastic flow at higher elongations. It is possible to stretch rubber so slowly that crystallites are not formed. Under such circumstances the tensile strength is greatly reduced<sup>6</sup>.

The molecularly ordered state brought about by the stretching of rubber is unstable when the stress is released. Thermal agitation then quickly results in a dissolution of the crystallites and a return of the molecules to the more probable random arrangement. This is accompanied by a rapid retraction and the return of the amorphous, relatively unordered structure<sup>7</sup>.

For rubberlike materials which do not form crystallites on stretching, we can be reasonably certain that a similar straightening and alignment of long-chain molecules occurs on stretching, with consequences similar to those in the case of natural rubber, although an actual crystal lattice is not formed. There must be some aspect to a rubberlike structure which prevents excessive slipping of the long-chain molecules on the application of stress. Otherwise, deformation would be of a plastic nature. This necessary rigidity can be introduced into the structure in a number of ways. The formation of crystallites, offering points of anchorage for the long-chain molecules, is only one possibility. Primary valence cross-linkages between the long-chain molecules appear to be the effective means in the case of many synthetic rubbers. In the case of vulcanized rubber, both mechanisms occur, and the relative effects of crystallite formation and cross-linkage in affecting the properties of vulcanized rubber is an interesting subject for experimental investigation<sup>8</sup>. In still other cases the secondary valence forces between the long-chain molecules may hinder plastic flow to a sufficient extent to give rise to high elasticity.

The formation of crystallites on stretching does occur in the case of several synthetic rubbers, proving that this characteristic is not necessarily related to the botanical origin of natural rubber. Patterns for unstretched and stretched Vistanex are shown in Figures 3 and 4. Such patterns were first reported by R. Brill and F. Halle<sup>9</sup>. The difference in structure indicated by the patterns is truly remarkable. Neoprene was the first synthetic rubber to exhibit

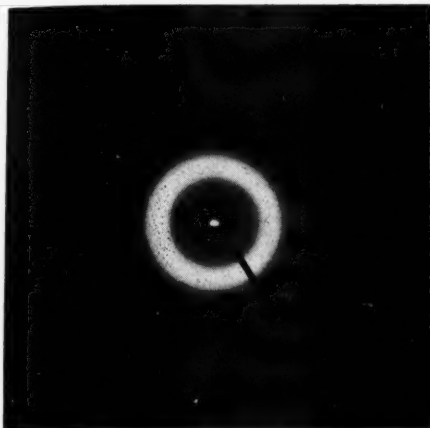


FIG. 3.—Vistanex unstretched.

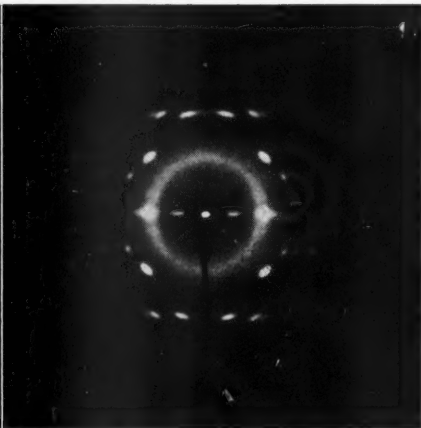


FIG. 4.—Vistanex stretched.

crystallinity upon stretching<sup>10</sup>. The degree of crystallinity, judged by the sharpness and intensity of the x-ray diffraction spots, appears to be less than in the case of natural rubber or Vistanex. Figures 5 and 6 are patterns for unstretched and stretched Neoprene, respectively. Some varieties of Thiokol

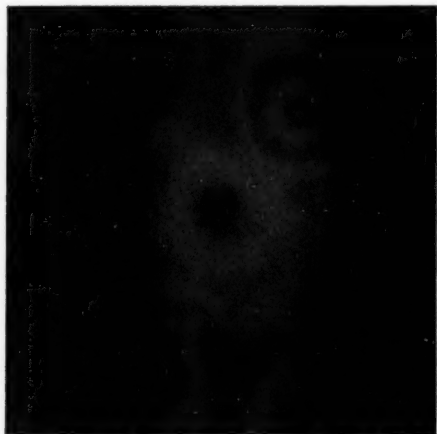


FIG. 5.—Neoprene unstretched.

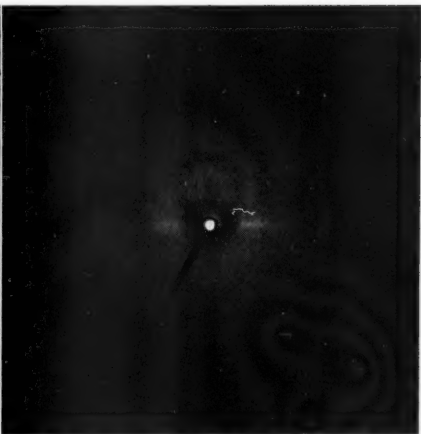


FIG. 6.—Neoprene stretched.

give crystalline fiber diagrams on stretching<sup>11</sup>. Figures 7 and 8 show the patterns of a commercial, vulcanized Thiokol stock, unstretched and stretched. Here the halo is possibly sharp enough to indicate some rudimentary crystallization. But there is no evidence of orientation.

The formation of crystallites on stretching, such as occurs in stretched rubber, Vistanex, and Neoprene, is apparently possible only when a uniform chemical structure exists in the long-chain molecules and when there are few,



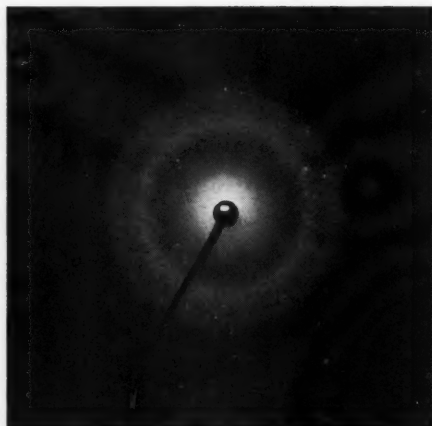
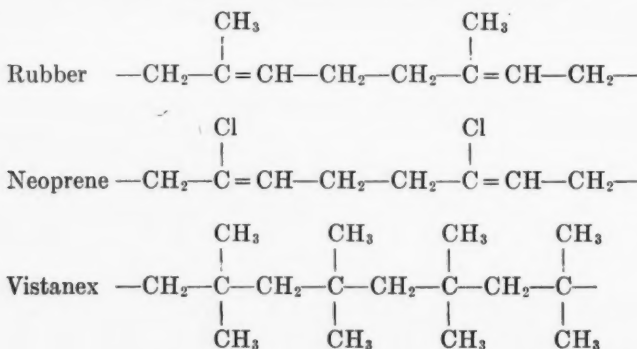


Fig. 7.—Thiokol unstretched.



Fig. 8.—Thiokol stretched.

if any, primary valence cross-linkages between the chains. The chemical formulas usually ascribed to these chain molecules are as follows:



The crystallization which occurs on stretching is evidence of the orderly arrangement of the methyl groups and chlorine atoms along the chains.

In the case of the polymerization of butadiene, amorphous products have always been reported<sup>12</sup>. As confirmed by the insolubility of the products, what evidently happens is an extensive cross-linking of chains. That is, instead of securing long chains (similar to those for rubber, but with the methyl groups replaced by hydrogen atoms), polymerization proceeds only until a chain of limited length is formed, and then a cross-linkage to a neighboring chain occurs at one of the double bonds. The uncontrolled character of these primary valence cross-linkages between the long chain molecules is presumably responsible for so much irregularity in structure that the formation of a crystal lattice on stretching is not possible. A number of synthetic rubbers are products of the copolymerization of butadiene and some other monomer or monomers. In such cases, it is most likely that, in addition to cross-linking, the monomers enter the chains in a random fashion, so the possibility of crystallization is entirely precluded.

Patterns for Buna-S and Buna-N are shown in Figures 9, 10, 11 and 12. The halo persists even at the highest elongation obtainable. In the case of a Buna-N tread stock, a splitting of the halo into two arcs was observed at higher elongations. This can be interpreted as being due to a high degree of alignment of the chain molecules in the direction of stretching, without the

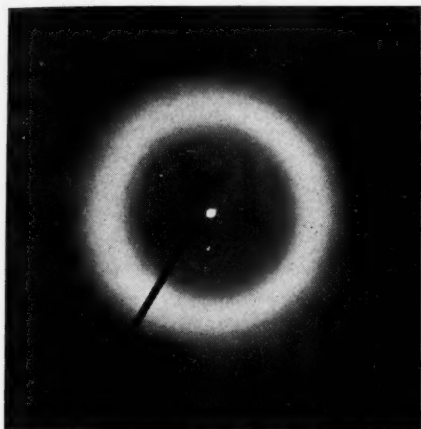


FIG. 9.—Buna-S unstretched.

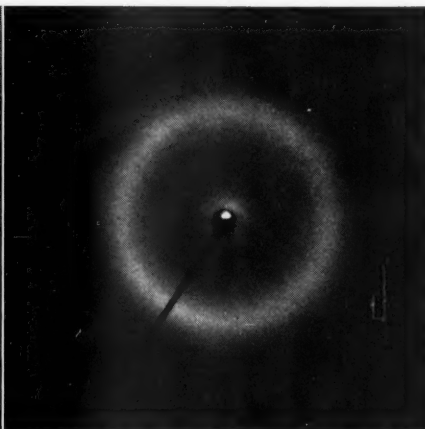


FIG. 10.—Buna-S stretched.

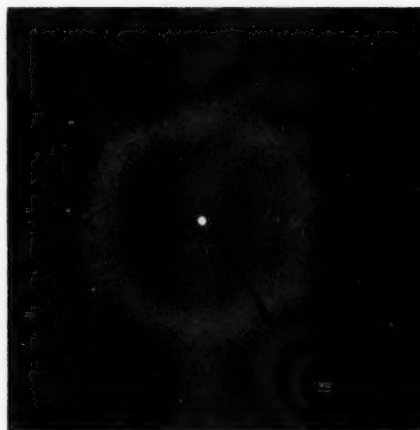


FIG. 11.—Buna-N unstretched.

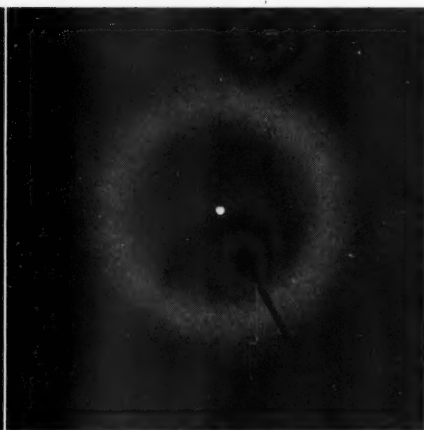


FIG. 12.—Buna-N stretched.

formation of a three dimensional lattice. The x-ray diagram of Chemigum (Figures 13 and 14) indicates the existence of an amorphous structure.

The formation of crystallites on stretching, such as occurs in natural rubber, is thus not a necessary characteristic for a rubberlike material, as has been previously explained. It occurs only under favorable conditions of regularity in the long-chain molecules. For the amorphous synthetic rubbers, information which can be obtained from x-ray patterns is very much limited, for they show simply a liquid structure. They do not reveal the molecular basis of

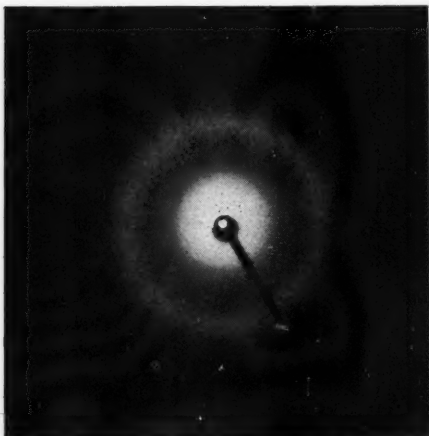


Fig. 13.—Chemigum unstretched.

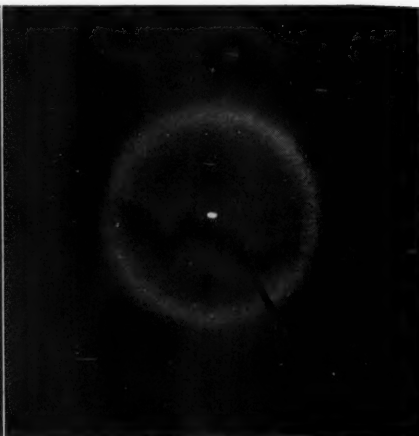


Fig. 14.—Chemigum stretched.

their rubberlike elasticity, that is, their capabilities of large extensions and retractions. This is now thought to reside in the straightening and alignment of long-chain molecules by stretching and the destruction of this relatively ordered arrangement by thermal agitation on release of the stress. Since the ordered arrangement produced by stress is not perfect enough to result in a crystal lattice, it does not become evident in the x-ray diffraction patterns. Only where crystallization occurs can the x-ray diffraction patterns be of much use in understanding the structure. Even then, a fundamental limitation of the x-ray diffraction method is that it gives information on the relative geometrical positions of the molecules, but none directly on the magnitude of the molecular forces involved.

From these considerations it is apparent that the structure of the synthetic rubbers is at least entirely different from that of natural rubber, and that they may owe their rubberlike properties to the operation of an entirely different mechanism.

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# THE SOLUBILITY OF SULFUR IN BUTADIENE-STYRENE COPOLYMER

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The solubility of sulfur in rubber has been studied sufficiently<sup>1</sup> for the various phenomena connected with solubility to be well known. Among the important factors are the available concentration of sulfur at any temperature, the diffusion of sulfur in the rubber<sup>2</sup>, blooming of both vulcanized and unvulcanized rubber, and the effect of supersaturation<sup>3</sup> on the formation of bloom. Similar studies have not been reported on synthetic rubbers which are vulcanized with sulfur. The present paper deals with the solubility of sulfur in a butadiene-styrene copolymer.

This work was conducted with a copolymer prepared from 75 parts of butadiene and 25 parts of styrene. The polymer contained about 6 per cent of acetone-extractable material, consisting largely of phenyl-naphthylamines and soap-forming acids, particularly stearic acid. It was the general type proposed for large-scale production, and was characterized by lack of tack, nerviness, and short break, especially when hot.

The general method employed was one already described<sup>3</sup>, and later employed in a modified form<sup>2</sup>. In general, it consists in the observation, with a low-power microscope, of known amounts of finely divided sulfur dispersed in rubber when very slowly heated and cooled in a hot stage. The solubility temperature is taken as the temperature at which all the sulfur disappears, and the limit of supersaturation is determined by the temperature at which the sulfur reappears when the rubber is slowly cooled.

It was found that the ordinary grade of rubber sulfur, when milled into the polymer, could not be observed satisfactorily. This is attributable to the almost complete lack of attraction between sulfur and the polymer. After long periods of milling above the solution temperature, much of the sulfur remained undissolved. When small pieces of the polymer-sulfur mixture were pressed between cover-glasses to a thickness of one to two thousandths of an inch, the polymer in many cases pulled free from the sulfur particle, and left a void extending from one glass surface to the other. If this action did not occur during the pressing operation, it occurred when heat was applied; the particle of sulfur remained either in the center of the void or clung loosely to one side of it. Under these conditions the sulfur could be heated to its melting point without dissolving in the polymer. When pressure was applied to the rubber just sufficient to prevent the polymer drawing away from the sulfur, the latter dissolved and left a void. Sufficient pressure, of course, caused the polymer to fill the void as the sulfur dissolved.

A master-batch method was finally employed for the incorporation of sulfur. One hundred parts of a polymer and 15 parts of sulfur were well mixed at a temperature above the melting point of sulfur. The hot mixture was then passed between the rolls of a cold rubber mill to chill it and to cause the sulfur to separate throughout the rubber in extremely fine supercooled droplets. Many of the droplets crystallized as such, while others migrated and formed fine dendritic or trichiten masses through the polymer. These

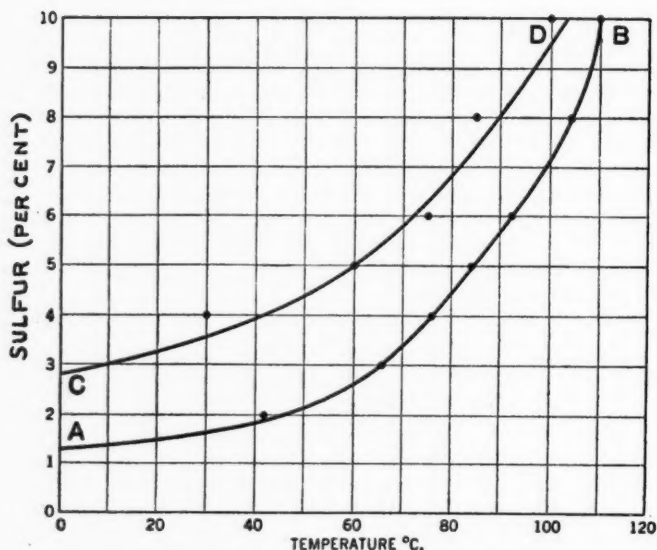
masses readily broke up during the milling operation and formed particles so fine that the polymer did not readily separate around them.

This master-batch of sulfur was used to prepare polymer with various proportions of sulfur, ranging from one gram in 100 grams of polymer to 10 grams in 100 grams of polymer. Pieces of each of these polymers the size of a pinhead were pressed thin between cover-glasses, and the cover-glasses and rubber were placed in the hotstage. The cover-glasses were supported by a coiled thermocouple, having the junction at the center. The heating current was adjusted so that heating and cooling was at the rate of about  $1^{\circ}\text{C}$  in five minutes near the critical temperature. A slow rate of temperature change was necessary because of the slow diffusion of sulfur through the polymer. The temperature at which the droplets disappeared on heating and reappeared on cooling are shown in Table 1, and are represented in Figure 1.

The droplets of supercooled sulfur, if undisturbed, may not crystallize for a considerable time, but if disturbed or seeded, crystallization begins at once.

TABLE 1  
SOLUBILITY AND LIMIT OF SUPERSATURATION OF SULFUR IN  
BUTADIENE-STYRENE COPOLYMER

Grams sulfur in 100 grams polymer	Solution temperature $^{\circ}\text{C}$	Limit of supersaturation $^{\circ}\text{C}$
2	42	—
3	66	—
4	76	30
5	84	60
6	92	75
8	104	85
10	110	100



A-B SOLUBILITY. C-D LIMIT OF SUPERSATURATION.

FIG. 1.—Solubility and limit of supersaturation of sulfur in Buna-S

In this case the action is the same as that described for rubber<sup>3</sup>. The super-cooled drops dissolve in the polymer and migrate toward the approaching crystal, which they serve to feed. The rate of crystal growth probably depends on the rate of solution and migration of sulfur through the polymer, and is a measure of the ease of uniform distribution of sulfur through the polymer. In the case of natural rubber, crystals grow easily at the rate of one millimeter per minute. However, in the butadiene-styrene polymer, the crystal growth is not more than 10 per cent so rapid as in rubber. This is due partly to the lower concentration of dissolved sulfur in the polymer, but in most part to the low rate of migration of sulfur through the polymer. This last point is proved by the low rate of extraction of crystals of sulfur from a block of polymer in comparison with the rate of extraction from rubber.

Since the solubility and diffusivity of sulfur in butadiene-styrene copolymer is lower than in rubber, it is more necessary, if uniform vulcanization is to be obtained, to assure good dispersion of more finely divided sulfur in the polymer. This is especially true of compounds containing large amounts of filler which retard the diffusion of sulfur. This can be accomplished by the use of master-batches prepared above the melting point of sulfur and cooled quickly.

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## THE PLASTICIZATION OF BUNA\*

HARRO HAGEN

Recently oxidative thermal softening of Buna has come to the fore, a process which has been called "degradation", a not too happily chosen term which suggests technical deterioration in quality. Properly speaking, there is loss in quality, just as there is considerable deterioration in quality when natural rubber latex is converted to dry rubber, a deterioration which is made still more extensive by mastication. Thus, while it is possible under laboratory conditions to make tread compounds having tensile strengths of 300-350 kg. per sq. cm. from natural rubber and latex compounds having tensile strengths of 450-500 kg. per sq. cm., the values obtainable with milled natural rubber are considerably lower. Despite this, one would not wish, except in the rarest instances, to dispense with the milling of natural rubber, since its processibility depends on the plasticization which is obtained by mastication.

Thermal softening of Buna-S corresponds to the mastication of natural rubber. It has been possible to produce treads of unsoftened Buna-S with tensile strengths of 300 to 320 kg. per sq. cm. from compounds prepared in the laboratory, but these results cannot be obtained on factory mills because of the poor dispersion of fillers. With thermal softening, the tensile strengths of tread compounds made on laboratory mills would, to be sure, be somewhat lower, viz., 280-290 kg. per sq. cm. In mechanical compounds, the improved dispersion of fillers, compared with unsoftened Buna-S, would cause an increase in tensile strength.

Oxidative softening is justified, not only from a processing and technical point of view, but above all because of the improvement in the finished product—provided, of course, that the degree of softening is suited to the intended application and that the optimum formula has been worked out. It would, therefore, be better to replace the derogatory word "degradation" by "oxidation" or "thermal softening".

### ADVANTAGES AND DISADVANTAGES OF OXIDATIVE SOFTENING

Compared with unsoftened Buna-S, thermally treated Buna-S has a number of advantages and disadvantages which will first be enumerated and then discussed. It is obvious that the change depends on the degree of softening, and a Buna-S that has been softened too much, like natural rubber that has been overmilled, is only of slight value in manufacture.

The chief disadvantages of thermal softening are as follows.

There is a decrease in the elasticity of the vulcanizate which can be corrected only with difficulty by compounding when softening has been carried to an advanced stage, and the working power of the vulcanizates declines. Buna-S is not so readily vulcanizable, and thus requires a higher percentage of sulfur and accelerator, and when this percentage is not carefully adjusted, aging, heat-resistance, and fatigue suffer. Greater care is, therefore, required in working out formulas.

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The advantages of thermal softening are as follows.

The power required for mixing, the mixing time, and the size of the pieces are the same as in the case of natural rubber. The capacity of the mills, therefore, remains practically the same when Buna instead of natural rubber is employed, so thermal softening reduces the cost of milling compared with that for untreated Buna. The dispersion of fillers is improved, so mixing is more complete, and there is less waste. The mixes can be more easily processed, and extrusion especially is facilitated. The tackiness of the compound is increased, although it still remains below that of natural rubber. Softening makes shearing in the cable industry possible. Where thermal softening eliminates the need of large amounts of softeners (plasticizers), there is an improvement in quality.

With more advanced degrees of softening, kneading machines can be used; kneaded compounds are very often considerably more favorable than milled compounds with respect to their final physical properties, but more especially with respect to facility of extruding and calendering.

The preparation of benzene solutions is facilitated because, without thermal softening, adequate solubility can be obtained only after very prolonged mastication. The viscosity of the solutions is lower and, therefore, higher concentrations can be used.

#### PROCESS OF OXIDATIVE SOFTENING

Softening is brought about by heating Buna in the presence of oxygen or air. The degree of softening is very materially influenced by four variables: temperature, time, air pressure, and rate of movement of the pieces of rubber. With the aid of catalysts which have not yet been put on the market, the rate of softening can be increased or the temperature reduced.

Relatively little is known about the chemical process in Buna rubber during thermal softening. It is certain that it requires oxygen; no softening takes place in steam or nitrogen. At the same time a part of the phenyl- $\beta$ -naphthylamine is sufficient to give the vulcanizate adequate protection against aging, and additional amounts of phenyl- $\beta$ -naphthylamine should be added to the mix only when it is to be subjected to especially severe demands. Accompanying the softening process, hardening of the Buna takes place; if Buna is heated in the absence of air, it slowly becomes harder, that is, it cyclizes, forms nets or vulcanizes without the addition of sulfur. This secondary reaction is, therefore, opposed to oxidative softening. Its rate increases with the temperature; hence the softening process should be carried out over short periods and at low temperatures.

#### METHODS OF MEASUREMENT

For the purposes of the present investigation, three methods of determining plasticity were considered. The determination of the viscosity of dilute solutions ran into difficulties because only a small softening interval is sufficiently soluble (see Figure 1). Measuring by the extrusion method after the Marzetti principle does not define the material exactly; the chief error lies in the sliding against the walls of the nozzles and of the nozzle opening. This value is not constant for identical degrees of plasticity. Therefore compression between platens with parallel faces and subsequent recovery were measured according to the Defo (deformation method) method developed by the Continental Caoutchouc G.m.b.H., which is the most satisfactory method.

Briefly, in this method, cylindrical test-pieces 10 millimeters high and 10 millimeters in diameter are compressed to four millimeters in 30 seconds at a temperature of 80° C. The force in grams required to do this is the Defo hardness, and is a measure of plasticity, which decreases as the Defo hardness increases. After a release period of 30 seconds, the height of the recovery (in 1/100 millimeter) is measured and shown in percentage of the original height of 10 millimeters. For example: 1500—70 indicates that to compress the test-piece to four millimeters in 30 seconds requires 1500 grams. In the next 30 seconds of release the test-piece recovers by three millimeters to seven millimeters. Materials thus considered to be without an elastic component have an "elastic portion" of 40 per cent, according to the definition.

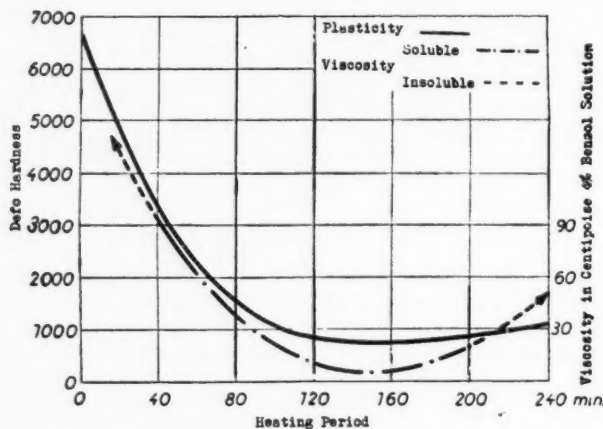


FIG. 1.—Plasticity and viscosity of 4% benzene solution, variation with softening time.

This method of measuring has now come into practical use, and about four degrees of plasticity are used:

Unsoftened Buna-S	Defo 7000
Slightly softened Buna-S for highly elastic qualities like carcasses	Defo 2000-3000
Medium soft, for abrasion-resistant qualities like treads, conveyor belts, etc.	Defo 600-1200
Very soft, for mechanical rubber goods, hard rubber, etc.	Defo 300-600

#### PLASTICIZATION OF BUNA BY THERMAL SOFTENING

At the present time, softening is carried out chiefly in double-jacketed vulcanizers, under pressure. The influence of time, temperature, pressure, and revolution of the material during softening, will now be discussed.

When Buna-S is treated by this method, the plasticity changes with the time of softening, as shown in Figure 1.

At first the Defo hardness decreases very rapidly, and the plasticity increases proportionately. At the same time the viscosity of a 4 per cent benzene solution decreases. After a minimum is reached, the Defo hardness and viscosity again increase. We shall call this minimum the resinification point, because the products resulting from continued thermal treatment lose a very consider-

able part of their adhesiveness and, when the heating periods are long, are hard, brittle, translucent substances, which are no longer soluble in organic solvents.

Evidently, then, oxidative softening is succeeded by a resinification or cyclization reaction which becomes predominant beyond the resinification point.

The plasticity of raw rubber or of a rubber mixture is defined as the ratio of the plastic to the elastic portion. Therefore if the elastic portion is plotted instead of the softening time (Figure 2), the internal processes become clearer. Then the resinification point appears as a point (Figure 2). When heating is continued beyond the resinification point, it is mainly the elastic portion of the plasticity which increases, while the extrusion and calendering qualities of the rubber deteriorate markedly. In thermal softening, care must be taken never to reach this point.

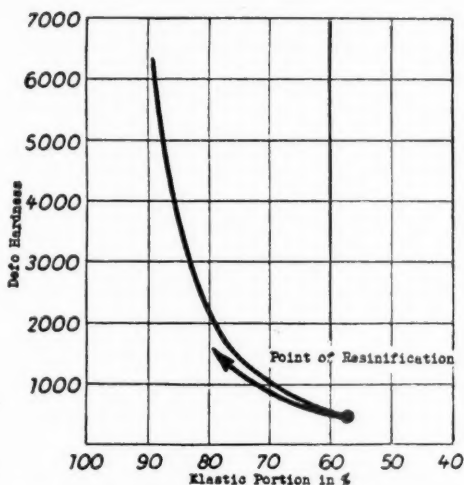


Fig. 2.—A typical change of the plastic-elastic conditions in thermal softening of Buna-S.

Figure 3 shows how temperature affects the rate of softening; the latter increases with the temperature; when the time is prolonged, plasticity differences are somewhat equalized; the danger of cyclization increases with the temperature; at lower temperatures the material shows greater uniformity, but elevated temperatures and short heating periods always lead to a mixture of various degrees of softening. For the sake of quality, the most uniform degree of softening possible is required. Therefore it is best, if possible, not to select softening periods under 30 minutes, for otherwise the steep part of the curve would have to be entered. For this reason and because of the danger of cyclization, the lowest possible temperatures should in practice be selected, especially when larger amounts of Buna have to be treated at one time. A longer softening period, moreover, gives better assurance of a constant temperature throughout the entire material.

On the other hand, the softening temperature must not be too low; as the 115-degree curve in Figure 3 clearly shows, the optimum possible plasticity

cannot be obtained at this temperature because, even before the point of degradation, the cyclization reaction has already canceled a part of the possible plasticization again so the resinification point is shifted to low plasticities. Independently of the softening temperature, however, practically identical products are formed before the resinification point, which is easily recognized when the Defo hardness is plotted against the elastic portion, as in Figure 4.

All the measuring points lie on the same curve; that is, the same softening conditions are passed through. The danger of resinification at excessive temperatures becomes evident.

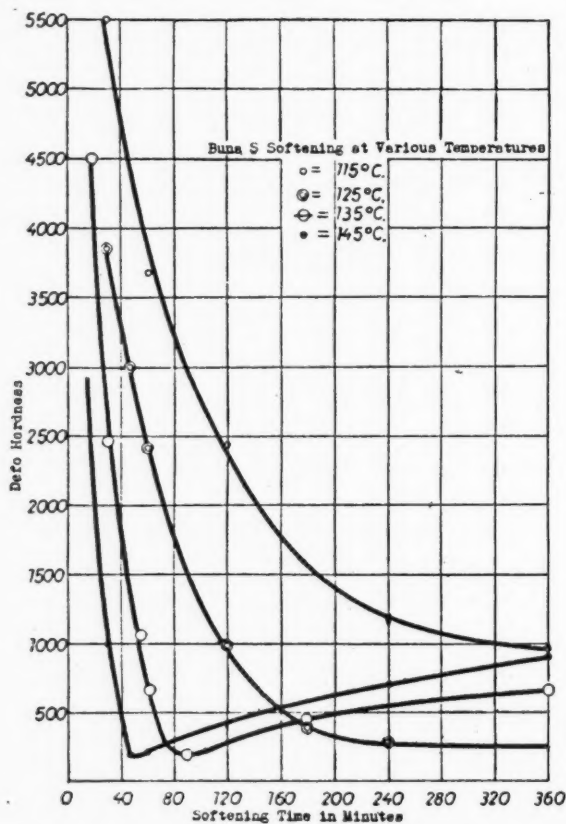


FIG. 3.—Effect of temperature on softening rate of Buna-S.

If the softening period does not exceed 30 minutes, then no further advantages can be had by an increase in temperature beyond a definite temperature. Figure 5 shows the results of softening at various temperatures. It is clear that the highest degree of softening is reached at 150 degrees, and that further increases in temperature merely increase the danger of cyclization.

The effect of pressure and revolution of the material during softening at constant temperature in a small vessel is demonstrated by the curve in Figure 6. Lower Defo values are obtainable with an air pressure of three atmospheres

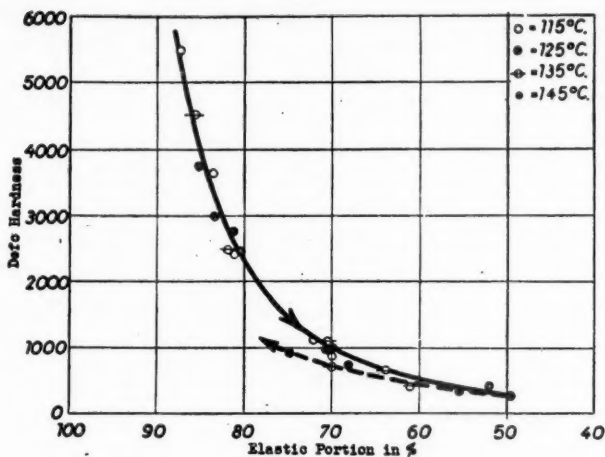


FIG. 4.—Softening conditions at various softening temperatures.

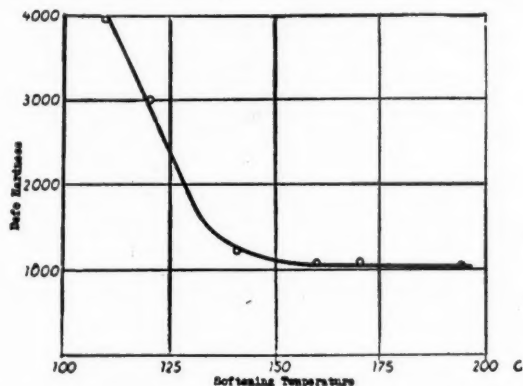


FIG. 5.—Thermal softening at various temperatures with a heating period of 30 minutes.

than without pressure. Although the effect of movement is less marked, yet by omitting the process, danger of resinification is increased. Above 180 minutes both of the curves without movement begin to mount again; that is, the resinification point is exceeded. Therefore the fullest possible use should be made of the favorable effect of air pressure and active movement.

That no really different products are formed in this case is verified by the curve of Figure 7, in which the elastic portion is plotted against the plastic portion. Apart from the usual variations, all points lie on one curve. Thus, independent of air pressure and circulation, Buna-S shows the same plasticity phenomena.

In addition to vulcanizers with air pressure above atmospheric, heaters for treating Buna have been used, in which Buna, either in the form of crumb or sheet, is loaded on racks and passed through the apparatus on rails. Compressed air is dispensed with; heated air is circulated instead. Any differences in temperature due to the apparatus are completely compensated by moving



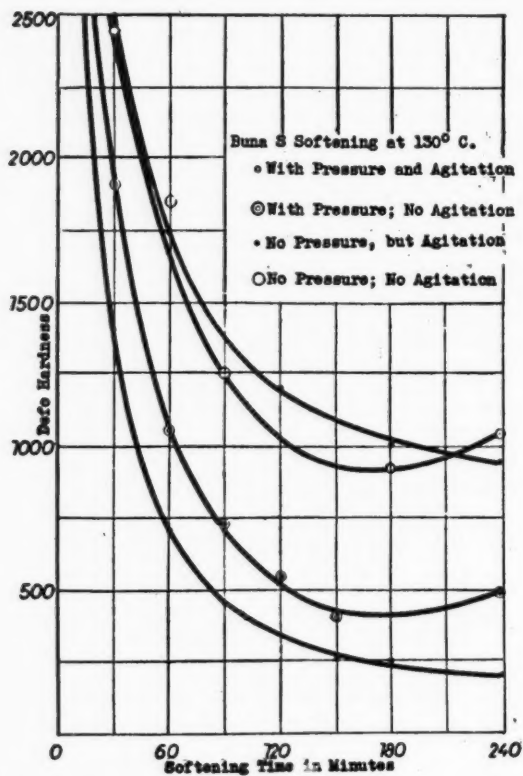


FIG. 6.—Effect of air pressure and turning over of material on thermal softening.

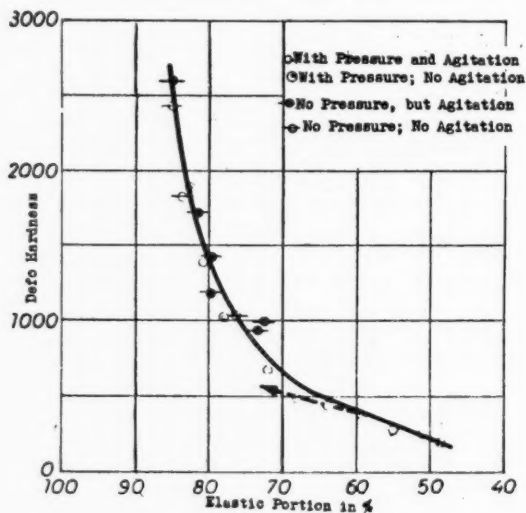


FIG. 7.—Results with various softening conditions.

the Buna through all the zones of the apparatus. Both methods and both forms of Buna (sheet or crumb) yield practically the same quality.

It is interesting to compare the softening of Buna-S crumb, the form in which it has hitherto been marketed, with Buna-S sheet, as it will be supplied in future. The form of Buna depends on the method of precipitation and drying, and has nothing to do with polymerization. The conversion from crumb to sheet has a number of advantages. Because of the method of preparation, crumbs are not of uniform size, but consist of small and large flakes, which render homogeneous softening difficult, since thorough oxidation of larger particles naturally takes longer than that of smaller ones. Furthermore crumbs stored for some time become caked and must be broken up before the softening process. On the other hand, sheet, lightly dusted with talc, can be easily unrolled at any time, and can be softened uniformly in layers of the same height. For uniform softening, crumb must be piled on racks to uniform height, but in the factory this piling is very difficult to achieve. Again, sheet is porous and holds air; hence uniform softening throughout its thickness can be counted on. If the softening rate of sheet and crumb are compared (Figure 8), crumb is found to soften somewhat more rapidly, probably because of its

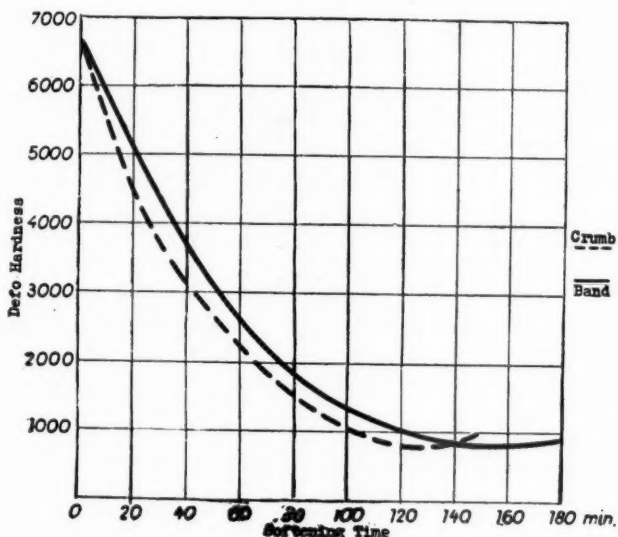


Fig. 8.—Comparison of the softening rate of Buna-S band and crumb.

large active surface. But uniformity in softening seems to be more important than speed so, for practical purposes, sheet is to be preferred.

If the plasticity of masticated Buna-S is compared with that of thermally softened Buna-S, it is found that the mastication periods and amounts of Buna treated are much less favorable, and the operation therefore more expensive than thermal treatment, as Figure 9 shows. At the same time, the amount of softened Buna-S depends on the size of the vessel. In a mastication test, 1500 grams was masticated on the laboratory mill, with rolls set together as closely as possible. If mastication were to be carried out on a factory scale

on factory mills, the mastication curve would be still flatter. In any case it is interesting to note that prolonged mastication results in somewhat different products than are obtained with thermal treatment. As Figure 10 shows, the

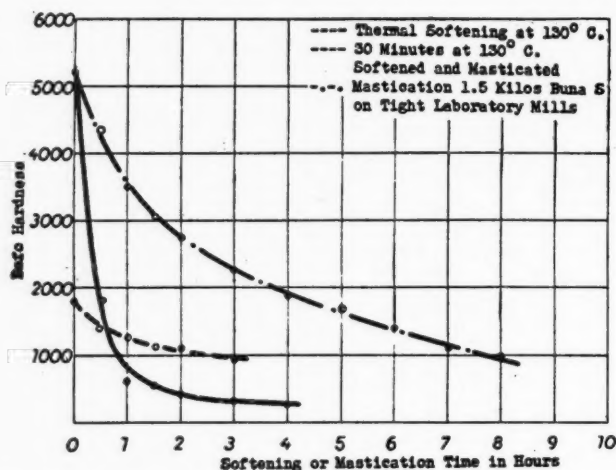


Fig. 9.—Comparison of mastication periods with softening periods of Buna-S.

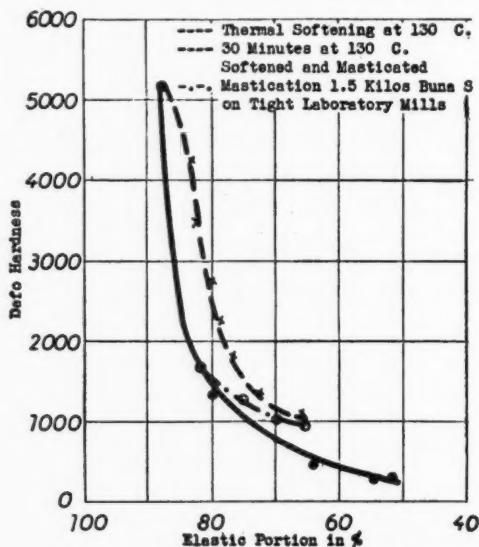


Fig. 10.—Changes in the elastic-plastic conditions of Buna-S during softening or mastication.

elastic portions and, hence, the extrusion and calendering qualities of the masticated material, are better than for material thermally softened to the same degree of plasticity.

It has not yet been found possible, either by means of additional ingredients or by changes in temperature and pressure, to move the softening curve of

pure Buna-S substantially to the right, that is, to achieve low elastic portions with the same degree of plasticity. Therefore the procedure is sometimes to masticate first and to follow by thermal softening, when the relatively pronounced milling qualities of the untreated Buna-S and the accompanying reduction in the elastic component, which is also retained in the succeeding thermal treatment, are exploited.

When certain catalysts are added in the proportion of about 1-2 per cent, by rolling them on or by spraying on both sides of Buna-S sheet, the softening rate can be substantially increased, as Figure 11 shows for two softening tem-

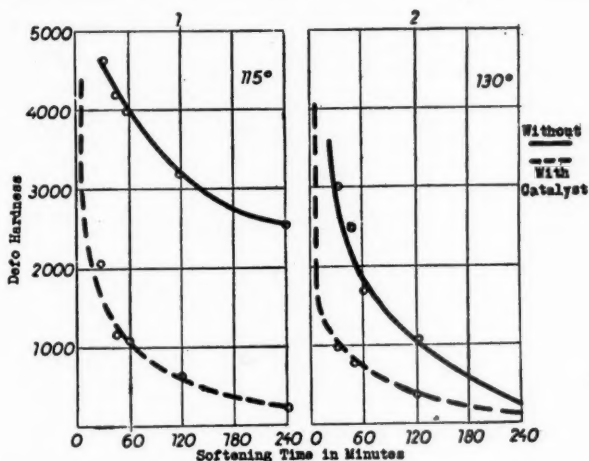


Fig. 11.—Effect of catalysts on the rate of softening.

peratures. As the original requirement of uniform softening of Buna (Figure 3) would call for treatment in the steep zones in this case and, hence, softening periods of less than 30 minutes, which would be inadvisable, acceleration of time cannot be achieved in practice by means of catalysts, but a reduction in temperature can be obtained, which may be of importance for power consumption in the future when large amounts of Buna-S are in use.

As far as present knowledge indicates, the products obtained differ in no respect from Buna-S softened thermally.

There are also catalysts which permit softening even at room temperature, but the question of price and certain other considerations are against their use. It is to be hoped that future developments will lead to the discovery of catalysts which are active at moderate temperatures and permit oxidative softening on hot rolls or in hot kneading machines so that mastication and mixing can be carried out as a single operation.

The storing qualities of thermally-softened Buna in the European climate, and as measured by the plasticity, are satisfactory. As with milled natural rubber, there is, in the first few days, a slight recovery which, on prolonged storage, tends asymptotically toward a final value. Simultaneously the solubility decreases, and the viscosity of the solution increases. At elevated storage temperatures, there is danger of a more marked internal cyclization, that is, hardening, with measurable increase of the Defo hardness, especially of the elastic portion, and eventual complete insolubility. Thermally softened

Buna-S that has become insoluble in storage can generally be easily rendered soluble again by brief mastication.

#### INDUSTRIAL PROPERTIES OF THERMALLY SOFTENED BUNA-S

The physical properties of the vulcanizates change as the degree of softening is raised; this is seen in its most exaggerated form on unfilled, transparent mixes (see Figure 12). The decline in tensile strength, loading, elasticity, and

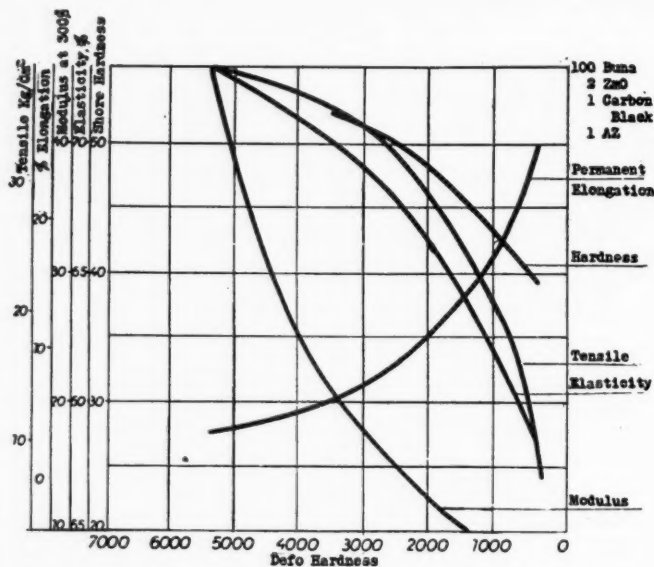


Fig. 12.—Changes in the physical values with increased softening: transparent quality.

hardness as the degree of softening increases is due to the decline in vulcanizability. As the permanent elongation indicates, the untreated Buna-S is overheated, and the curves prove once more that vulcanizing agents must be suited to the degree of softening.

In the present academic formula, even careful adjustment of sulfur-accelerator result in marked improvement of tensile strength and elasticity under certain conditions only. In the case of lightly filled mixes, of course, extreme softening can be dispensed with. On the other hand, the effect of softening on the usual Buna-carbon-black mixes is not so marked. The same conditions will, therefore, be demonstrated on a tread (see Figure 13).

The composition of the mix has in this case too been kept constant. Here too, we recognize the decreased vulcanizing facility by the rise in the permanent elongation and the decrease in the load. This decrease in load is due also to improved dispersion of the carbon black, especially in the low plasticity zone (where little softening has taken place). This improved carbon dispersion is responsible for the increase in tensile strength at a low degree of softening, whereas the sharp drop in tensile strength with high degree of softening is due partly to undercuring, and can to some extent be corrected by higher doses of vulcanizing ingredients, and the same is true to correct the decrease in elasticity. Below a Defo hardness of 600, increases are usually no longer possible,

just as in natural rubber that has been dead-milled. However, it is possible to obtain tensile strengths of 150 kg. per sq. cm.

Figure 13 makes it clear also why highly elastic qualities with a low degree of softening are acceptable. It is not until the Defo hardness falls below 2500–3000 that there is a noticeable loss in elasticity. In the case of tread com-

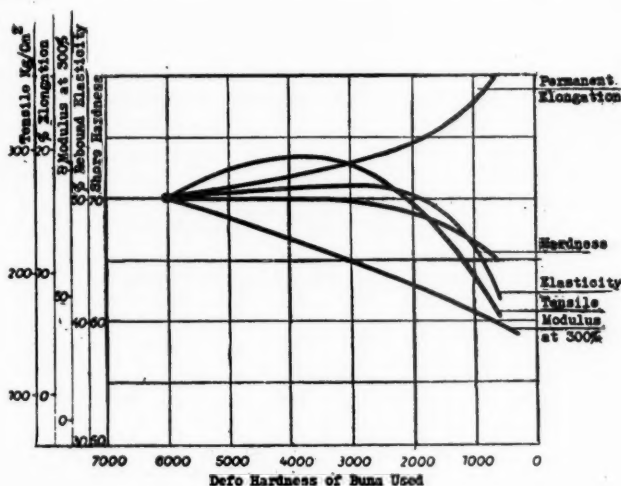


FIG. 13.—Changes in the physical values with increased softening: tread quality.

pounds, a slight decline can be tolerated, and consequently the softening process can be continued.

Thus, for softened Buna-S, the formula must be adapted to the degree of softening, especially the proportions of sulfur and accelerator. No softener was added to the two unsoftened compounds, as shown in Table 1. The

TABLE 1  
CONVEYOR BELT COMPOUND

	Buna-S		Natural rubber
	Not softened	Softened	
Rubber	100.0	100.0	100.0
Carbon black	42.0	42.0	42.0
Stearic acid	2.0	2.0	2.0
Ozokerite	1.5	1.5	1.5
Sulfur	1.3	2.2	2.6
Vulkacit-AZ	1.2	1.2	0.9
Cumar resin	12.0	—	—
Rosin	5.0	—	—
Kautschol	5.0	—	—
Mineral oil	5.0	—	—
Zinc stearate	5.0	—	—
Test Results			
Tensile (kg. per sq. cm.; lbs. per sq. in.)	200(2850)	250(3560)	280(3990)
Elongation (percentage)	480	600	580
Elasticity (percentage)	44	45	50
Shore hardness	73	70	70



changes in quality were still more marked in the case of a compound with high softener content. Thermal plasticization permits, or necessitates, as the case may be, a decrease in the percentage of softener, and so the formulas become increasingly more like those usual for natural rubber, as the table for a conveyor belt compound shows.

As in the present example, an improvement in quality can be achieved by softening if the proper degree of softening is selected, while the time for mixing is shortened, and larger volumes can be handled on the mill. In practice, however, it is not possible to dispense with softeners altogether, even in the above compound, and even when the Buna-S is considerably softened, for the higher elastic portion, compared with natural rubber, continues to be responsible for unsatisfactory extrudability. To clarify this, a masticated natural rubber is compared with a thermally softened Buna-S.

Figure 14 shows the difference in the plasticity conditions of softened

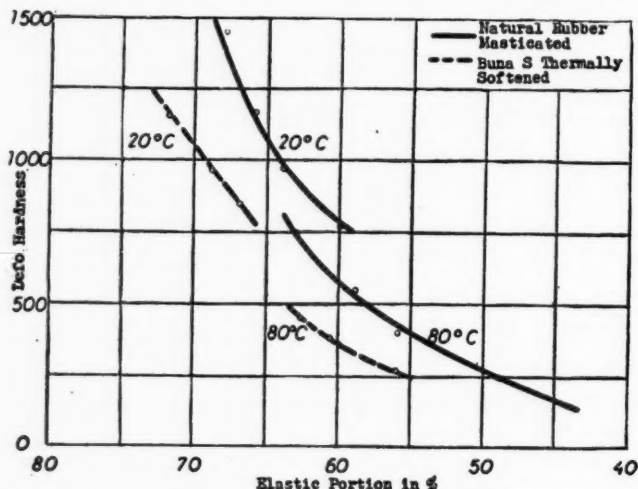


FIG. 14.—Comparison of the plastic-elastic condition of oxidation softened Buna-S and masticated natural rubber at 20° and 80° C.

Buna-S and natural rubber at 20° and 80° C, with very low Defo values. With the same plasticity, rubber has a lower elastic portion and thus shows less tendency to shrink; that is, it is more easily and smoothly extruded and calendered. To obtain the same plasticity conditions as in natural rubber, the addition of substances to improve extrusion, as wool fat, wool wax, low polymer numbers Buna, softener oil, etc., can hardly be avoided.

The undesirable loss in elasticity caused by thermal softening can in part be compensated by stiffer vulcanizates. This is all the more necessary since the elasticity of a compound that has not been thoroughly vulcanized changes unfavorably with the temperature. Thus the decline in elasticity in Figure 13 would be still more abrupt if the elasticity had been measured at the high temperatures found in tires.

Figure 15 shows that, in the case of untreated Buna-S, the rebound elasticity (measured with the Schob pendulum-hammer) rises slightly with the temperature. On the other hand, the elasticity of very soft Buna-S drops with the temperature when there is undercuring. The elasticity does not re-

main constant with increasing temperature until curing is complete. In the example in Figure 15, varying degrees of vulcanization are produced by means of sulfur; because of the other properties of vulcanizates such as aging, fatigue, etc., this is not permissible in practice to the same degree, but the dependence of the working capacity on the degree of vulcanization is more convincingly proved than if changes in accelerator had been made. The composition of the compound, especially the proportion of accelerator, has thus been kept constant, except for the sulfur content. The curves show clearly that the elasticity measurement at 20° C does not reflect adequately the actual changes in quality. Thus, to determine working capacity, measurements should take place at about 70° C.

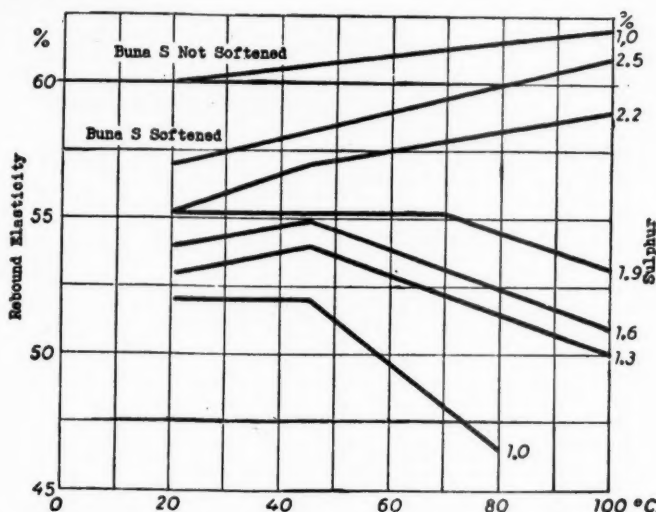


Fig. 15.—Dependency of the temperature coefficient of elasticity on the degree of vulcanization.

Furthermore it becomes clear that sufficient vulcanization is necessary, especially to improve the working capacity (strength). Hence accelerator doses must be selected which are safe in the early stages of vulcanization, but at the same time give as thorough and rapid a cure as possible. In a large number of tests the accelerator, Vulkacit-AZ, proved consistently to be the most suitable for this purpose. At the same time the percentage of sulfur is increased compared with unsoftened Buna-S, but this increase must be made with care because of the aging properties, especially resistance to aging in heat, which will be illustrated on a tread compound.

Industrial tread compounds of untreated, and of very soft thermally treated Buna-S, practically free from softeners, were aged. The formulas differ only with regard to the sulfur content, which was 1 per cent for the unsoftened and 2 per cent for softened Buna (Table 2).

In the case of the softened Buna-S, the aftercure, that is, the increase in load and hardness, deteriorated especially in the 70° Geer oven. The excessive increase in the amount of sulfur must be held chiefly responsible for this. For, if a less steep increase in sulfur content is selected, and at the same time the accelerator content is increased, aging can be brought back to practically the original level, as Table 3 shows.

TABLE 2  
BUNA-S AGING

Aging (days)	Not softened		1% sulfur			Very soft		2% sulfur		
	F	D	B	E	H	F	D	B	E	H
0	225(3200)	690	38(540)	54	65	203(2900)	670	52	50	68

Geer 70° C oven

8	230(3280)	540	74(1055)	56	72	210(3000)	475	106(1515)	54	77
16	236(3380)	525	86(1225)	57	75	204(2900)	420	121(1725)	53	78
32	228(3250)	510	99(1410)	56	76	180(2560)	300	141(2010)	54	79

Bierer-Davis  
Bomb 60° C

8	227(3240)	675	54(770)	54	72	198(2820)	570	81(1155)	52	73
16	225(3210)	640	61(870)	55	75	196(2795)	540	90(1280)	51	76
32	211(3010)	640	67(955)	56	76	180(2560)	500	105(1495)	53	78

F = Tensile strength (kg. per sq. cm.; lbs. per sq. in.).

D = Elongation (percentage).

B = Modulus (kg. per sq. cm.) (lbs. per sq. in.).

E = Rebound elasticity (percentage).

H = Shore hardness.

TABLE 3  
BUNA-S AGING

Aging (days)	Very soft Tensile strength (kg. per sq. cm.; lbs. per sq. in.)		1.2% Sulfur Elongation (percentage)		1.5% Vulkacit-AZ Modulus (kg. per sq. cm.; lbs. per sq. in.)	
0	230(3280)		720		30(427)	

Geer 70° C oven

8	235(3350)	530	61(870)
16	238(3390)	510	80(1140)
32	240(3420)	500	91(1295)

Bierer-Davis  
Bomb 60° C

8	234(3330)	690	45(640)
16	228(3250)	630	57(815)
32	200(2845)	560	69(985)

Clearly then, the decrease in elasticity and vulcanizability, resulting from the softening process, should be compensated, not only by increasing the sulfur content, but by changing the content or type of accelerator at the same time. Under these conditions the elasticity or working power of even very soft, thermally treated Buna-S can be improved, although the level of untreated Buna can hardly be reached.

Thermal oxidation softening plays about the same part in the processing of Buna-S that mastication does with natural rubber. But we are still only at the beginning of a technical development, so the present contribution should be considered as a process that is still in the developmental stage, and it must be emphasized that, while oxidative softening is a substantial advance in the problem of processing Buna, it has not yet been able to make Buna-S similar to natural rubber. The proper use of thermal softening demands a very high sense of responsibility in producers of rubber goods because, in the effort to obtain good processibility, too high a degree of softening is likely, and the resulting inferiority of the finished goods would shake confidence in synthetic rubber.

## EFFECT OF TEMPERATURE ON RESILIENCE OF NATURAL AND SYNTHETIC RUBBER\*

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The necessity of the substitution of synthetic elastomers for natural rubber has been forced on the rubber compounder by the exigencies of war. His background of a hundred years of research and compounding is his principal weapon for making this conversion in the shortest possible time. Too often he finds that this background fails and that practices invaluable in the development of natural rubber stocks are worthless in the case of synthetic rubber, or at least are subject to a different interpretation.

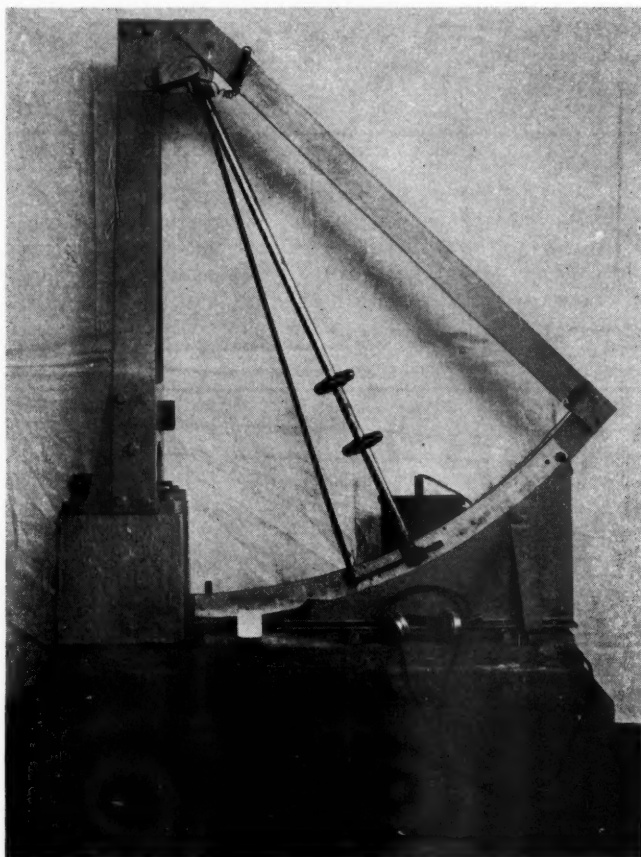
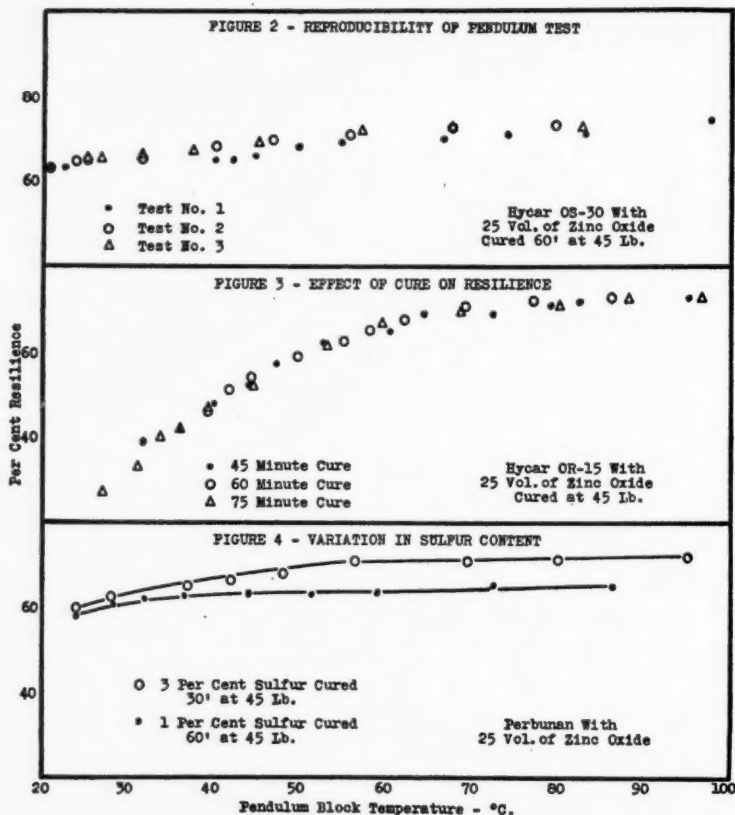


FIG. 1.—Goodyear-Healey type of pendulum.

\* Reprinted from the *India Rubber World*, Vol. 108, No. 2, pages 137-140, May 1943.

One such difference is the subject of this report. The published work of this and other laboratories<sup>1</sup> has shown that resilience of a rubber compound, as measured by a pendulum of the Goodyear-Healey type<sup>2</sup>, illustrated in Figure 1, can be correlated with the heat generated during flexing on an apparatus such as the Goodrich flexometer. This made it possible to use the pendulum as a rapid test indicative of the value of a stock designed for heavy-duty service.

That this relation would exist with synthetic elastomers appeared a likely assumption. Early in the work, however, exceptions were noted, and the investigation of these resulted in at least a partial explanation of the reason why hysteresis, measured by these two methods, is not always in agreement.



Although the resilience and heat-generating characteristics of the several synthetic elastomers may vary considerably, they are all poorer than natural rubber. The deficiency has caused considerable attention to be directed toward the compounding of stocks for applications where flexing and heat generation are important factors in the service life of the article. Most synthetic elastomers are more critical toward thermal effects than natural rubber, and these effects are manifest in stress-strain and tear-resistance measurements at elevated temperatures, as well as in hysteresis effects.

The comparison of two stocks, one compounded with Hycar OS-30, a butadiene-styrene copolymer meeting the specification (in effect November, 1942) for GR-S; the other compounded with Hycar OR-15, butadiene-acryloni-



trile elastomer, showed that the pendulum resilience of the former was nearly twice that of the latter. However, heat build-up tests on the Goodrich flexometer and flexing to failure on the Firestone flexometer reversed this order, and the best performance was obtained with Hycar OR-15. The most obvious difference between the two tests is that the pendulum measures hysteresis loss at room temperature, whereas the flexing tests are affected not only by room temperature hysteresis, but also by hysteresis at the elevated temperature during the flexing test. Examination of the temperature-rise data of the Goodrich flexing test shows that, at the start of the test, the heat build-up per minute of flexing for the Hycar OR-15 stock is greater than for the Hycar OS-30 stock. However, after the temperature of the test-piece reaches 55° C, the reverse is true, and the heat build-up per minute of flexing is higher for the Hycar OS-30 compound. This suggested a study of the resilience over a range of temperature covered by the flexometer tests.

#### EFFECT OF VARIOUS FACTORS ON PENDULUM TESTS AT 0°-100° C

In these experiments, six synthetic elastomers and natural rubber were compounded in gum stocks and with 25 volumes of zinc oxide, and were tested for resilience on the Dunlop-type pendulum in a range of temperatures from 0 to 100° C. A fine wire iron-constantan thermocouple of the type employed in tire temperature measurements was inserted in the pendulum block (2 inches by 2 inches by 1 inch) half-way between the top and the bottom and about 1/2-inch in from the side, in a position that did not interfere with the impact of the pendulum hammer. The pendulum blocks were heated in an oven at 110° C for one hour; then they were mounted in the pendulum, and temperature measurements were taken periodically as the block cooled to room temperature. So that the test-sample would not cool down too rapidly, the anvil of the pendulum was preheated with a reflecting type of electric heater. The temperature range from 0° C to room temperature was determined after the block had been cooled in a refrigerating unit to about -10° C, and resilience measurements were made as the block warmed up to room temperature.

The reproducibility of the pendulum test under the conditions of this investigation is shown in Figure 2, in which the results of three duplicate runs on a Hycar OS-30 stock compounded with 25 volumes of zinc oxide are in close agreement. This degree of reproducibility of the resilience measurements is typical for the other elastomers examined.

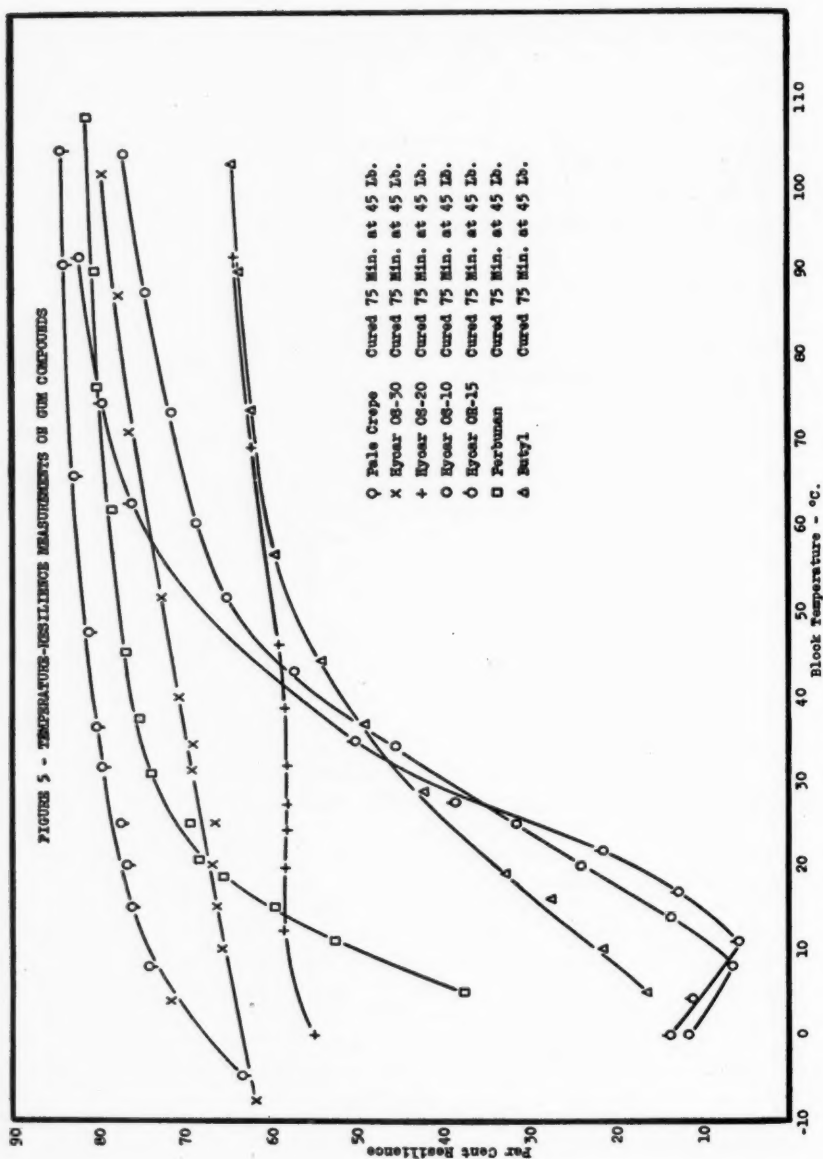
The state of cure of a 25-volume zinc oxide Hycar OR-15 compound over the range of 45 to 75 minutes at 45 pounds (144.5° C) did not influence the temperature-resilience characteristics of this stock (Figure 3). These results were representative of the effect of cure determined for the other compounds. Obviously if the curing range were extended, the resilience would be affected.

Some idea of the influence of compound modification on the temperature-resilience curve is indicated in Figure 4, in which data are plotted for 1 and 3 per cent sulfur loadings in Perbunan, pigmented with 25 volumes of zinc oxide. The compound with 3 per cent sulfur has a somewhat higher resilience than the 1 per cent sulfur stock; however, the shape of the temperature-resilience curve for both sulfur contents is the same. In the series of elastomers and natural rubber compounds, all the stocks were compounded with 3 per cent sulfur except Butyl rubber with 2 per cent sulfur and the 25-volume zinc oxide Hycar OR-15 compound with 4 per cent sulfur.

#### REBOUND AND HARDNESS—PURE-GUM AND PIGMENTED STOCKS

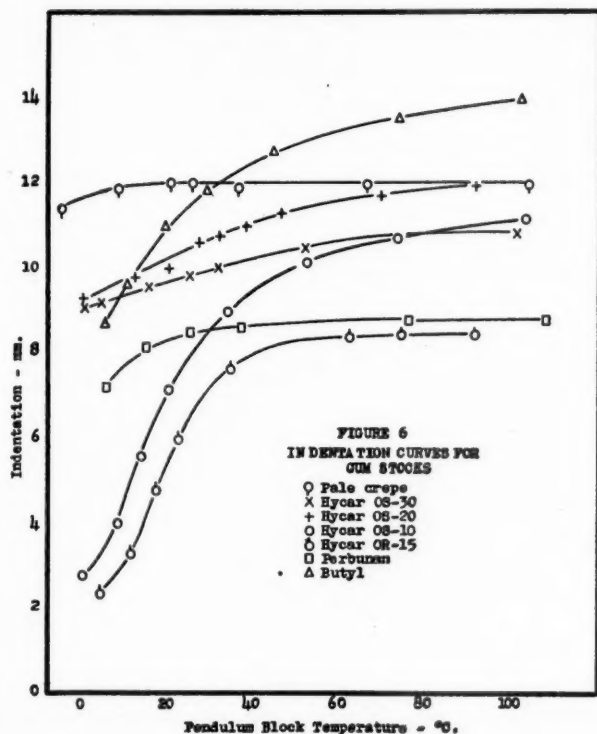
The synthetic elastomers and natural rubber were compounded in gum stocks, and pendulum measurements were determined at comparable cures.





An optimum cure or slight overcure was selected for the comparison. The pendulum measurements in Figure 5 show that natural rubber develops the highest resilience, and that there is a relatively slight change in resilience over the temperature range investigated. Hycar OS-30 also has a flat or "plateau" type of temperature-resilience curve, but exhibits a lower resilience than natural rubber. It is notable that Hycar OS-20, a copolymer similar to Hycar OS-30 except for fat acid and soap content (Hycar OS-20 is essentially free of fat acid; Hycar OS-30 has 3-6 per cent fat acid) had a temperature-resilience curve that also was very flat, but the resilience was lower than that of Hycar OS-30. Perbunan and Hycar OR-15 developed very high resilience at elevated temperatures, but became much less resilient at lower temperatures. This thermoplastic tendency was also exhibited by Butyl rubber and Hycar OS-10, although the loss of resilience at low temperature was not so great with Perbunan as with Hycar OR-15, Hycar OS-10, and Butyl rubber. The inflection point on the low temperature end of the Hycar OR-15 and Hycar OS-10 curves, indicating an increase in resilience beyond this point, cannot be explained.

Indentation or dynamic hardness measurements of the gum compounds are plotted in Figure 6. These values were determined on the pendulum resili-



ometer at the same time as the resilience measurements by means of a vernier stud which contacted the lower hammer on the pendulum arm. Hycar OR-15 had the highest dynamic hardness, Butyl rubber the lowest. The slopes of the temperature-indentation curves of the several elastomers were in fair agreement with the curves showing temperature *vs.* resilience.



The most striking difference between the temperature-resilience curves of the gum stocks and the corresponding curves of the 25-volume zinc oxide compounds (Figure 7) is that the pigmented natural rubber compound had a distinctly higher resilience than the pigmented synthetic elastomers. A closer study of the curves in Figures 5 and 7 shows that, in the temperature range of 90–100° C, a 25-volume loading of zinc oxide lowers the resilience only slightly below that of the unloaded natural rubber compound. There is a lowering of less than 5 per cent in rebound in the case of Hycar OS-30 and Hycar OS-10, and less than 10 per cent in the case of Perbunan and Hycar OR-15. The Butyl rubber and Hycar OS-20 compounds, however, were in the reverse order, *i.e.*, the pigmented stocks were more resilient than the gum stocks. When the evaluations were made at 30° C, the resilience of the pigmented and gum stocks agreed within 2 per cent in the case of pale crepe, Hycar OS-10, and Hycar OS-20; Hycar OS-30, Butyl, Perbunan, and Hycar OR-15 showed greater reductions with pigmentation. The general characteristics of the curves of the pigmented stocks were essentially the same as the curve of the gum compounds, including the inflection points on the low temperature end of the Hycar OR-15 and Hycar OS-10 curves. The superior resilience of Hycar OR-15 to Hycar OS-30 in the temperature range from 70 to 100° C explains the Goodrich flexometer results mentioned previously, in which Hycar OR-15 had better flexing properties than Hycar OS-30.

Indentation measurements for the 25-volume zinc oxide compounds had the characteristic contour of the corresponding gum compounds, but the values were somewhat lower because of hardness which had been induced by pigmentation.

#### DISCUSSION OF RESULTS

From the foregoing experiments and from what is known of the chemical composition of the elastomers, several interesting observations can be made. Except for natural rubber, the best low-temperature resilience was exhibited by the elastomers high in butadiene content, *viz.*, Hycar OS-30, Hycar OS-20, and Perbunan. The inferior low-temperature resilience of Hycar OS-10 and Hycar OR-15 can be ascribed to the high percentage of styrene or acrylonitrile in these elastomers. These data suggest that polymers high in styrene and acrylonitrile are thermoplastic and have relatively poor low-temperature resilience properties. Indications are, however, that both of these materials have very good resilience at elevated temperatures. It is recognized that resilience is only one factor involved in service performance, and the effect of styrene and acrylonitrile on other properties must be considered in any final interpretation of these data. Apparently the fat acid present in Hycar OS-30 (3–6 per cent) improves the resilience of this elastomer, for it has a higher resilience than Hycar OS-20, which is presumably the same as Hycar OS-30 except that it is essentially free of fat acid.

A meager explanation of the observed data is made, because of a lack of fundamental background as to the structure and composition of the several elastomers studied, and it is offered as a contribution to knowledge of compounding synthetic elastomers. It is planned to continue this investigation at both low and high temperatures, and to attempt to correlate hysteresis with other physical properties and attempt to isolate the factors which govern both the shape and position of the temperature-resilience curve.

#### REFERENCES

- <sup>1</sup>Barnett and Mathews, *Ind. Eng. Chem.*, **26**, 1292 (1934).
- <sup>2</sup>Jones and Pearce, *Proc. Rubber Tech. Conf. London*, 1938, p. 830.

# A METHOD OF TESTING THE ELASTICITY OF SYNTHETIC RUBBERS AT LOW TEMPERATURES\*

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With the appearance of many new synthetic rubber compounds, the need has arisen for quick and practical testing to determine their comparative applicability to uses formerly filled by natural rubber compounds. One of the most important points is the elastic behavior of synthetic rubbers at low temperatures, and such information is imperative when synthetics are to be introduced into the design of a new product. To obtain accurate data, an instrument termed an *Elastensometer* was devised.

## PRINCIPLE OF THE ELASTENSOMETER

The principle of the instrument is illustrated diagrammatically in Figure 1. Utilization is made of the fact that the modulus of elasticity of rubberlike

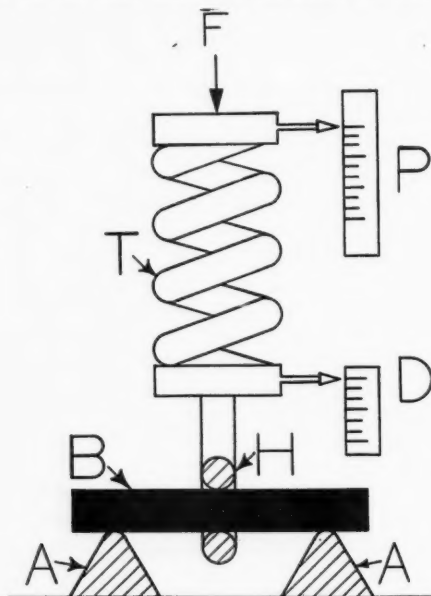


FIG. 1.—Diagrammatic illustration of the operating principle of the elastensometer.

materials in general varies inversely with temperature. A specimen is supported in the form of a simple beam B, 0.290 inch diam.  $\times$   $1\frac{1}{2}$  inches long, freely supported over anvils AA and centrally loaded at H. The force F required to produce a given constant deflection D is transmitted through spring T and is indicated on scale P. Knowing the value of F at intervals of temperature as the temperature of the test-bar is dropped, a force-temperature curve

\* Reprinted from *The Rubber Age* of New York, Vol. 53, No. 2, pages 131-135, May 1943.

can be plotted. The critical limit of normal elastic properties is reached at the temperature at which the force required to produce constant deflection increases rapidly.

Figure 2 is a photograph of the Elastensometer. A dial indicator is connected directly to the loading rod and shows the deflection in thousandths of an inch. Loading is applied with a hand-lever, and is transmitted to the test-bar by a double-wound spring. Calibration of the loading spring (Figure 3)

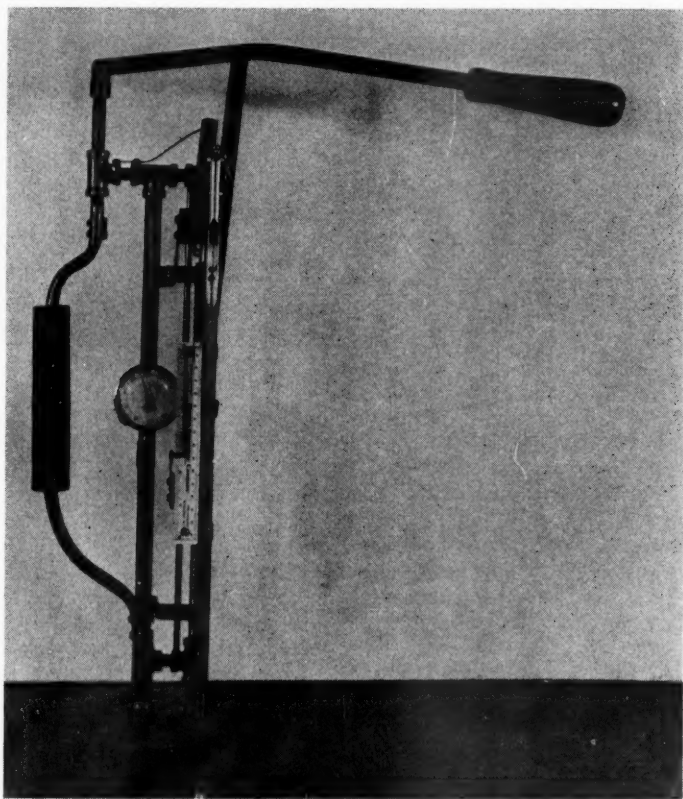


FIG. 2.—Full view of the elastensometer.

for values indicated on the vertical scale was made directly by unscrewing the anvil plate and mounting the instrument on a pipe fixture over the platform of a weighing scale. A suitably encased thermometer is mounted close-grouped with the deflection dial and force scale for easy reading of all three. The instrument weighs less than 5 pounds, and is designed to be supported in the left hand while being operated with the right.

A lay-out of the complete equipment required for testing is illustrated in Figure 4. This includes the Elastensometer, insulated cup, splash-pan, cracked dry-ice, alcohol, a hollow cutter for making 0.290 inch. diam.  $\times 1\frac{1}{2}$  inches long test-specimens, spoon for handling the dry-ice, and tongs for inserting the test-specimen into the anvils.



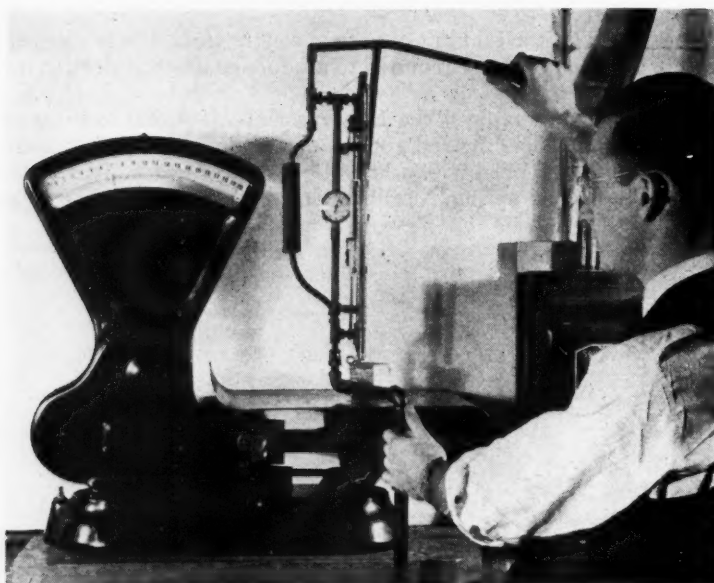


FIG. 3.—Calibration of the loading spring.

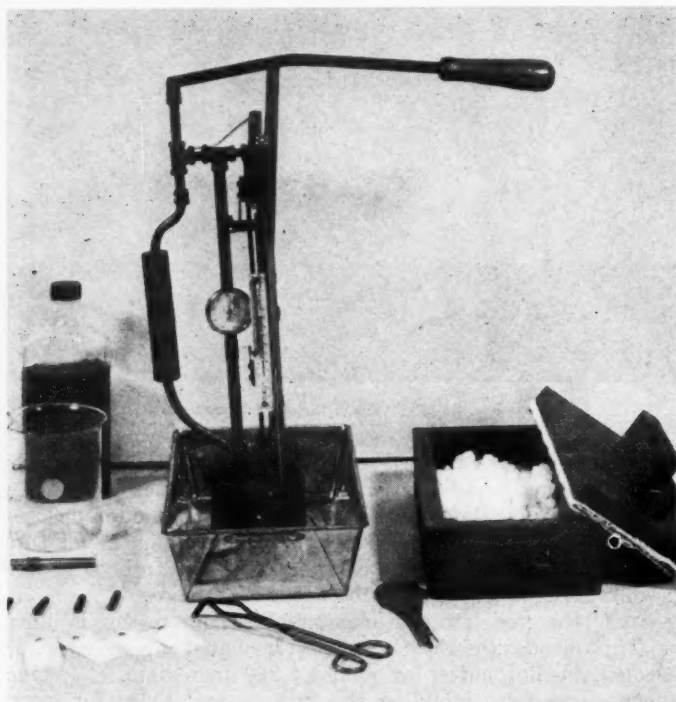


FIG. 4.—Complete equipment required for making the low-temperature test includes the elastensometer, insulated cup, splash pan, box of cracked dry ice, alcohol, beaker, hollow cutter, test-specimens, forceps, and spoon.

## METHOD OF CONDUCTING TESTS

To conduct a test, the sample is inserted into the anvil (Figure 5) and through the looped end of the loading rod; since one inch of the  $1\frac{1}{2}$  inch length is unsupported,  $\frac{1}{4}$  inch support is obtained on each anvil, and the test-bar is prevented by means of removable pins from slipping out. Testing is begun with the base of the instrument immersed in a cup of alcohol at room temperature. The technique of the test is to apply a sufficient load with the hand

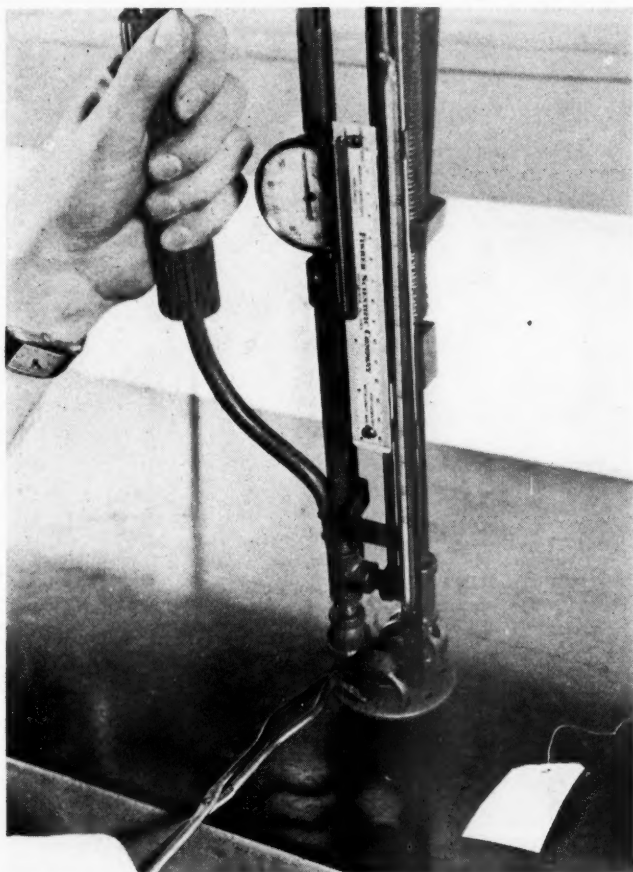


Fig. 5.—Method of inserting a test-specimen into the supporting anvils of the elastensometer.

lever to produce a given deflection; the indicated force and temperature are then noted and the load is allowed to return to zero. This process is repeated at suitable intervals as the temperature is carefully lowered by the addition of small quantities of dry ice to the alcohol until the desired low temperature is obtained. Stirring is accomplished as required by raising and lowering the instrument, thus allowing the coolant to flow through holes in the base plate.

The Elastensometer was designed to provide economy of time and material and ease of operation. The first consideration was to achieve simplicity in

preparation of the test-specimen. This is accomplished by cutting the specimen with a hollow cutter operated in a drill press (Figure 6). By this method, uniform, cylindrical pieces, 0.290 inch diam.  $\times$   $1\frac{1}{2}$  inches long, can be produced from any part of a plaque of the compound. The anvils (AA in Figure 1) are placed to give free support at a distance of one inch apart; this helps to simplify calculations. If desired, a numerical value of the modulus of elasticity in bending can be determined for any temperature, since testing can be conducted even when the material is brittle. Tests at high temperatures can be conducted by use of a heated cup with or without an immersion fluid. The

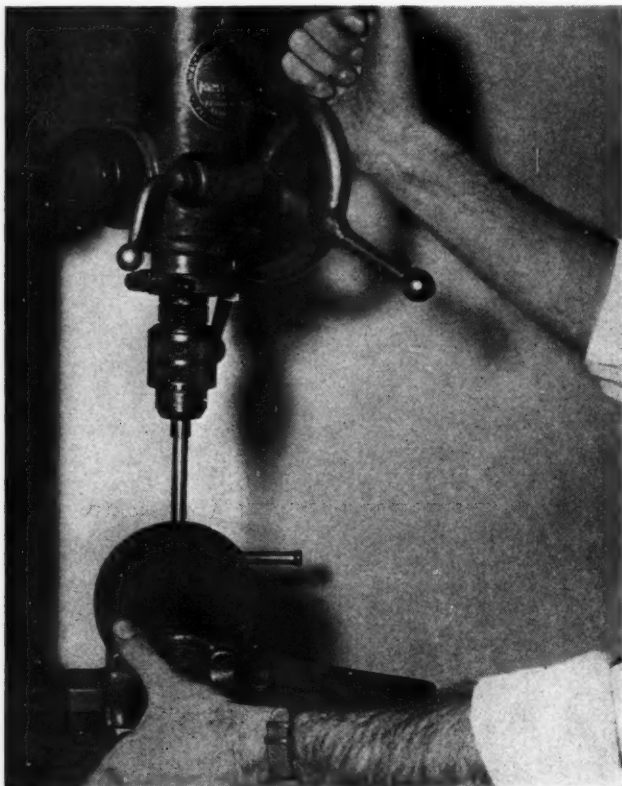


FIG. 6.—Cutting a test-specimen with a hollow cutter in a drill press.

operational base of the device, together with the test-specimen, is compact enough to permit immersion in an insulated cup of only 300 cc. capacity. A further advantage is that comparatively small forces are required, as opposed to tensile pulling, which makes for a light, easily handled and hand-operated instrument.

Figures 7 and 8 give the results on two different compounds of like characteristics at room temperature, but differing widely at low temperatures. In each case two curves are represented, showing the effects of different values chosen for deflection  $D$ . To provide quick comparative results, the same deflection must be applied to all tests. Points X and X' on the curves indicate

the critical limit, determined by inspection. The critical limit is that temperature at which the modulus of elasticity begins to increase at a rapid rate. By plotting the force required to produce a constant deflection against temperature, the first sudden change of curvature indicates the critical limit.

Factors affecting the choice of deflection  $D$  are:

(1) The maximum value which does not cause a permanent set at the testing temperatures, remembering that the modulus of elasticity tends to increase as the temperature is lowered.

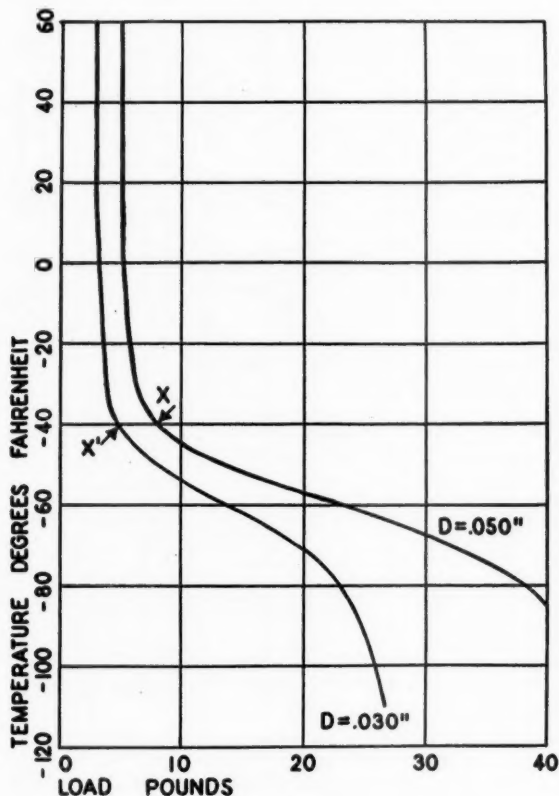


FIG. 7.—Test results of a typical safe low temperature material.

(2) The minimum value which shows a marked change of curvature at the critical values of temperature. If  $D$  is too small, significant points on the curve may escape visual detection.

In general, the maximum value of  $D$  which does not cause a permanent set, *i.e.*, exhibit negligible time-lag in achieving full recovery, is used. A  $D$  value of 0.050 inch has been found to be of ample range for practically all commercial synthetic rubbers produced thus far where the critical limit is of chief interest. For studies considerably below the critical limit, a smaller value, as for example,  $D = 0.030$  inch is used.

A descriptive scale of interpretation may be applied to the  $D = 0.050$  inch curves as follows:

0 to 8 lbs.	Flexible
8 to 15 lbs.	Semi-Flexible
15 to 22 lbs.	Firm
22 to 30 lbs.	Hard
30 to 40 lbs.	Brittle

Descriptive scales of elastic behavior for other values of  $D$  below the critical limit are, in general, chiefly dependent on the nature of the application. Where

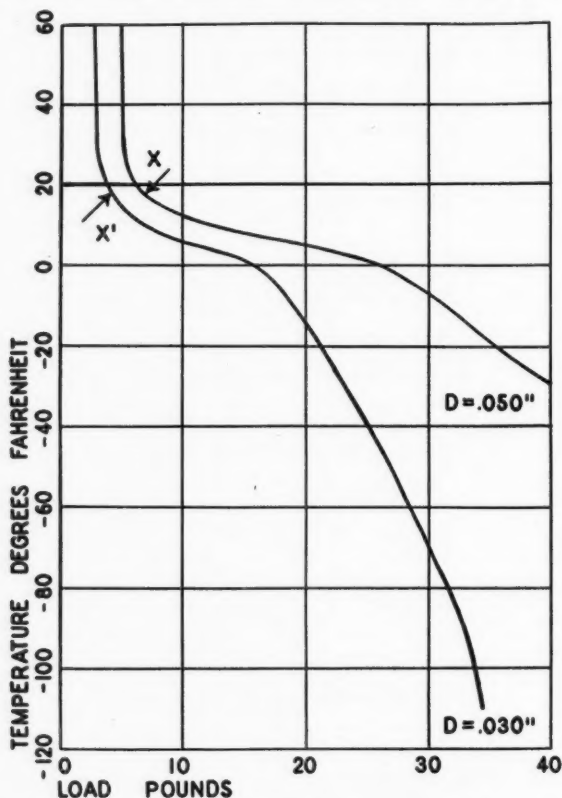


FIG. 8.—Test results of a material whose critical temperature is above 0° F.

the material is almost completely confined, as is the case with Dresser coupling gaskets, the semiflexible state is in the safe zone. For such applications as automobile tires, for example, where there is no confinement and the material is directly exposed to wear, the critical limit would probably define the safe temperature limit, and might require closer definition.

The modulus of elasticity  $E$ , in bending, at any temperature may be obtained by use of the conventional beam deflection formula:

$$E = \frac{PL^3}{48ID} \quad (1)$$

where  $P$  is the load in pounds (applied gradually),  $L$  is the length (1'),  $I$  is the moment of inertia of the cross-section about the neutral axis ( $0.04909d^4$ ), and  $D$  is the deflection (in inches).

Since the modulus of elasticity in bending,  $E$ , tends to increase as the temperature is lowered (Figure 9), the limiting critical temperature, obtained with the Elastensometer, may be closely defined as that temperature where

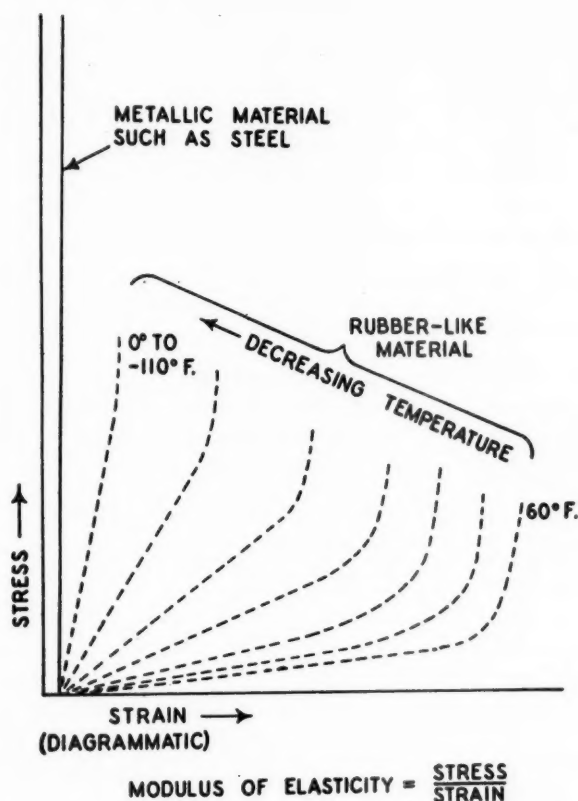


FIG. 9.—Diagrammatic illustration of the changing values of the modulus of elasticity of a rubberlike material with decreasing temperature.

the normal value of  $E$  increases to the maximum value permitted for the application. For materials exhibiting given elastic characteristics at normal temperatures, the tolerable deviation at the limiting temperature may be specified in percentage of increase in  $E$ . For example, rewriting Equation (1):

$$E = K \frac{P}{D} \quad (2)$$

where

$$K = \frac{L^3}{48I} \quad (3)$$



Using the values plotted in Figure 7 for a test-specimen whose diameter is 0.290 inch:

$$K = \frac{1}{48 \times 0.04909 \times 0.290^4} = 60, \quad (4)$$

and a table of values may be constructed as follows:

TABLE OF VALUES

Temp. (° F)	<i>E</i>	% Increase of <i>E</i>
60 <sup>±20*</sup>	6,000	0
-20	7,200	20
-37	8,400	40
-40	9,600	60†
-45	12,000	100
-57	24,000	300
-68	36,000	500
-85	48,000	700

\* Taken as normal. † Typical critical limit selected by visual inspection: Points X and X', Figure 7.

Although the critical limit may thus be specified mathematically, determination by visual inspection is usually adequate. Good results may be obtained with comparatively large tolerances on the diameter of the test-specimen.

Tests made with the Elastensometer have been found convenient and inexpensive to conduct, and no great outlay of equipment is required. A sample compound can usually be tested in thirty minutes, including the time required for cutting the test-specimen in a drill press.

## CUT GROWTH OF BUNA-S COMPOUNDS\*

### A METHOD TO DETERMINE THE RATE OF CUT GROWTH OF BUNA-S COMPOUNDS

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Buna-S vulcanizates do not flex-crack in the same manner as do those of natural rubber. As long as the surface remains unmarred, the resistance to flex-cracking is excellent, but when the surface is impaired by cuts or light checks, failure due to the growth of the cut takes place rapidly. This type of failure is a serious one, causing premature failure of such goods as tires and conveyor belts flexed in service. Since none of the usual methods for measuring flex-cracking of natural rubber vulcanizates gave satisfactory results with Buna-S, it became necessary to develop a test-method before means of alleviating or overcoming this defect could be developed.

#### APPARATUS AND TEST METHODS

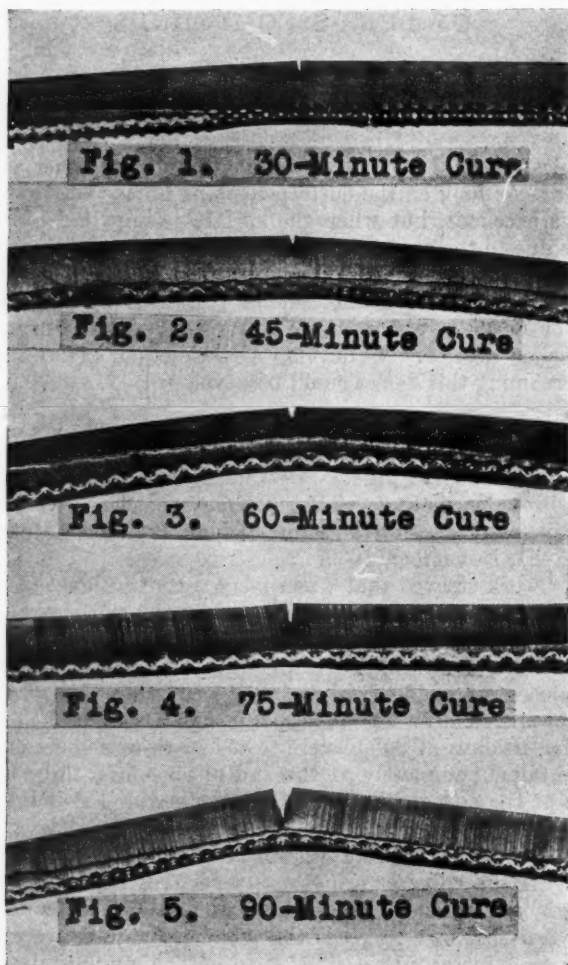
The apparatus used was the du Pont flexing machine, as made by Henry L. Scott Co., Providence, R. I. This machine and the method of operation are described in A.S.T.M. Standards on Rubber Products (Method C-D430-35T), pages 78-81, November, 1939.

Preliminary work showed that when unaged conventional test-pieces were used, failure occurred where they were pierced by the belt hooks after running 10-20 hours at room temperature. This failure was overcome by moulding a one-inch wide strip of a natural-rubber tread stock at each end of the test-piece. Unaged test-pieces prepared in this manner were run 175 hours without the development of cracks. Twenty identical test-pieces which had been aged in a Geer oven for 10 days at 80° C were tested, with extremely erratic results. One test-piece failed completely at the end of 55 hours, three at the end of 94 hours, two at the end of 124 hours. At the end of 153 hours, nine of the test-pieces showed no cracking, while five test-pieces showed varying degrees of cracking. Obviously such data were of no value.

To investigate the value of using test-pieces that had been nicked with a razor blade, a mould was made to the same dimensions as the du Pont mould for preparing test-specimens, except that the corrugations were omitted and the thickness was increased to 0.275 inch. The unvulcanized stock was allowed to rest 16 hours after mixing and then, after being backed with a layer of frictioned belt fabric, was moulded and cured with the grain perpendicular to the 7½-inch side of the slab. The smooth cured slab, 4 by 7½ inches, was then cut into test-pieces one inch wide and four inches long, the grain being parallel to the four-inch side. A razor blade cut was made across the test-pieces equidistant from the ends. Preliminary work showed that a cut 0.040-inch deep gave consistent results and rapid cut growth. This depth of cut has been used throughout the work covered by this report.

\* Reprinted from the *India Rubber World*, Vol. 108, No. 2, pages 141-142, May 1943.

Since Buna-S vulcanizates show a decided loss in tensile strength and resistance to tearing with increase in temperature, the authors felt that cut growth should be measured at elevated temperature as well as at room temperature. Tests at elevated temperatures should tie in better with service



Showing effect of state of cure on flex crack growth for compound E, flexed three hours at 180° F.

results, since tire treads, conveyor belts, etc., run at temperatures well above those of the surrounding atmosphere.

An oven was built around the pulley assembly of the du Pont machine. Heat was supplied by means of electric strip heaters, and circulation was obtained by means of a baffle and fan. Temperature was automatically controlled by a Mercoid switch. The top of the oven contained a window so that the progress of the test could be observed without removing the test-pieces.

With the oven at the desired temperature, the test-pieces were placed on the pulleys and allowed to remain at rest for 30 minutes before starting the test. A test was stopped as soon as one test-piece cracked nearly through to the fabric. The depth of the crack was measured at the two sides of the test-piece by means of a low-power microscope, having a graduated ocular, and the two readings were averaged. Three test-pieces were used for the final data. The thickness of the test-piece between the bottom of the cut and the top of the fabric was 0.195-inch. Cut growth data was expressed in percentage of this total thickness (crack depth divided by 0.195). A flexing temperature of 180° F was found to give sufficiently rapid crack growth for good results.

#### COMPARISON OF NATURAL RUBBER, NEOPRENE-GN, AND BUNA-S

The compounds shown in Table 1 were compared for rate of cut growth, both at room temperature and at elevated temperature. The results obtained are set forth in Tables 2 and 3.

TABLE 1

SMOKED SHEET, NEOPRENE AND BUNA S COMPOUNDS USED FOR STUDY OF CUT GROWTH

	A	B	C	D	E
Smoked sheet rubber	100.	....	....	....	....
Neoprene-GN	....	100.	100.	....	....
Buna-S*	....	....	....	100.	100.
Wyex channel black	50.	36.8	31.	50.	50.
Zinc oxide	5.	5.	5.	5.	5.
Magnesia†	....	4.	4.	....	....
Sulfur	2.75	....	....	2.	2.
Stearic acid	4.	1.	1.	2.	2.
Pine tar	2.5	....	....	....	....
Barrett D.O. No. 10	....	....	....	10.	....
Turgum‡	....	....	....	....	10.
Circo light oil	....	1.	1.	....	....
Latac	....	0.1	0.1	....	....
Mercaptobenzothiazole	0.875	....	....	1.	1.
Di-o-tolylguanidine	....	....	....	0.2	0.2
Benzothiazyl disulfide	....	0.25	0.25	....	....
Phenyl-β-naphthylamine	1.5	....	....	....	....

\* Hycar OS-30. † Extra-light calcined. ‡ Refined turpentine gum.

TABLE 2

Cure* (min.)	Flexed 36 hours at 82° F			Flexed 7 hours at 82° F	
	A	B	C	D	E
30	(†)	None	None	33%	3%
45		None	None	46	4
60		None	None	55	10
75		None	None	63	10
90		None	None	70	15
105		None	None	..	15
120		None	None	..	8

\* Compound A cured @ 274° F. Compounds B, C, D, and E cured at 287° F. The optimum cures follow: A = 60 min. B and C = 45 min. D = 60 min. E = 90 min.

† See text.

*Flexing at Room Temperature.*—Compounds A, B, and C were flexed 36 hours at room temperature (82° F). At the end of this period, Compound A containing natural rubber developed cracks unlike those developed by Buna-S compounds in that they were not perpendicular to the surface of the test-

TABLE 3

Cure (min.)	Flexed 11 hours at 180° F			Flexed 50 min. at 180° F		Flexed three hours at 180° F E
	A	B	C	D	E	
30	25%	37%	76%	12%	9%	30%
45	29	49	36	42	6	31
60	37	32	48	89	8	47
75	44	35	52	100	7	63
90	55	56	71	100	6	76
105	..	..	..	...	7	89
120	..	..	..	...	19	100

piece, but turned at an angle and, in some instances, were nearly parallel to the test-piece surface. No doubt this condition is caused by the so-called "knotty" structure of a natural rubber-carbon black compound. No appreciable differences were noted for the 30-, 45-, 60-, 75-, and 90-minute at 274° F cures.

Compounds B and C containing Neoprene showed no cut growth at the end of the 36-hour flexing period, and were much superior to natural rubber.

*Flexing at Elevated Temperature.*—When flexed at 180° F, the cracks in all compounds were perpendicular to the surface of the test-piece. This shows that, at this temperature, natural rubber no longer exhibits a "knotty" structure.

Compound B, containing Neoprene and 36.8 parts carbon black (equivalent to 50 parts on 100 parts rubber), is approximately equal to Compound A containing natural rubber. Compound C, containing Neoprene and 31 parts carbon black, is inferior to Compounds A and B with respect to cut growth.

Compound D, containing Buna-S and a coal-tar softener, shows extremely poor cut growth resistance. Compound E, containing Buna-S and an acidic-type softener, is far superior to Compound D, but is decidedly inferior to either natural rubber or Neoprene.

State of cure has a radical effect on the rate of cut growth of Buna-S compounds. Note the rapid increase in rate of cut growth of Compound D with increase in time of cure, particularly when tested at elevated temperature. Also note the sudden increase in rate of cut growth of Compound E between the 45-minute and 60-minute cures when flexed three hours at 180° F (see Figures 2 and 3). When flexed at room temperature, Compound E shows very little difference between the various cures, but when flexed at elevated temperature, rate of cut growth increases with time of cure.

#### CONCLUSIONS

1. A satisfactory laboratory method has been developed for measuring the rate of cut growth of Buna-S compounds.
2. Buna-S compounds are inferior to both natural rubber and Neoprene with respect to rate of cut growth.
3. Cut growth measurements made at elevated temperatures give entirely different results from those made at room temperature.
4. State of cure has a radical effect on the rate of cut growth of Buna-S compounds; the undercures are superior to normal cures or overcures.

## SOME OBSERVATIONS ON THE FLEX-CRACKING CHARACTERISTICS OF GR-S (BUNA-S) COMPOUNDS\*

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Probably the most serious defect of GR-S rubber is its poor resistance to flex-cracking, and much research has been conducted in an effort to improve this characteristic. Among the many tests employed in the study of rubber is the bend-flexing method, using the De Mattia apparatus, as described in A.S.T.M. Method D430-35T. However, when GR-S vulcanizates were flexed according to the standard procedure, erratic results were obtained.

In an effort to secure more reproducible test data, a study was made of the crack growth that proceeded from small nicks made initially in the surface of the sample. Some difficulty was encountered in making a nick of uniform dimensions until a procedure was developed whereby a pinhole about 0.025 inch in diameter and approximately 0.05 inch deep was made in the center of the grooved surface of the test-piece. The hole was made by a pointed piece of steel, shielded so that it could penetrate the sample only to a constant depth. When the samples were prepared in this manner, the crack growth which extended from the hole during flexing was fairly uniform, and the results were reproducible within rather close limits.

Many different compounds were flexed in accordance with this technique at room temperature, and it was noticed that the rate of crack growth was affected particularly by the state of cure and by the degree of loading of the stocks; the tighter the cure and the higher the loading, the more rapid the crack growth. The choice of accelerators and sulfur ratios apparently had little effect, provided the state of cure was the same in each case.

Since GR-S rubber is more brittle at elevated than at room temperatures, it was decided to conduct tests at 100° C. For this purpose, the De Mattia apparatus was enclosed within an insulated case containing electric strip heaters and an electric fan to provide adequate circulation of the heated air.

Many compounds were tested at the higher temperatures, and it was discovered that some which had not cracked too badly in 50,000 flexes at room temperatures failed completely in about one-tenth of the time when flexed at 100° C. In general, the results at 100° C confirmed those obtained at room temperature.

In the course of experimentation it was discovered that the addition of 10 to 20 parts by weight of "hard" clay to a normal GR-S carcass or tread resulted in a decided improvement in the flex life of the stocks. This improvement was evident also when the clay was added to Perbunan or natural-rubber stocks. The improvement is illustrated in the accompanying photos.

The influence of the state of cure and the temperature of flexing on the flexing life of a medium-loaded GR-S stock that might be used as a carcass stock is illustrated in Figure 1. Compound A, in this case, contains 15 parts

\* Reprinted from *The Rubber Age* of New York, Vol. 53, No. 4, pages 331-334, July 1943. This paper is essentially that presented at a meeting of the New York Rubber Group, Division of Rubber Chemistry, American Chemical Society, New York, June 11, 1943.



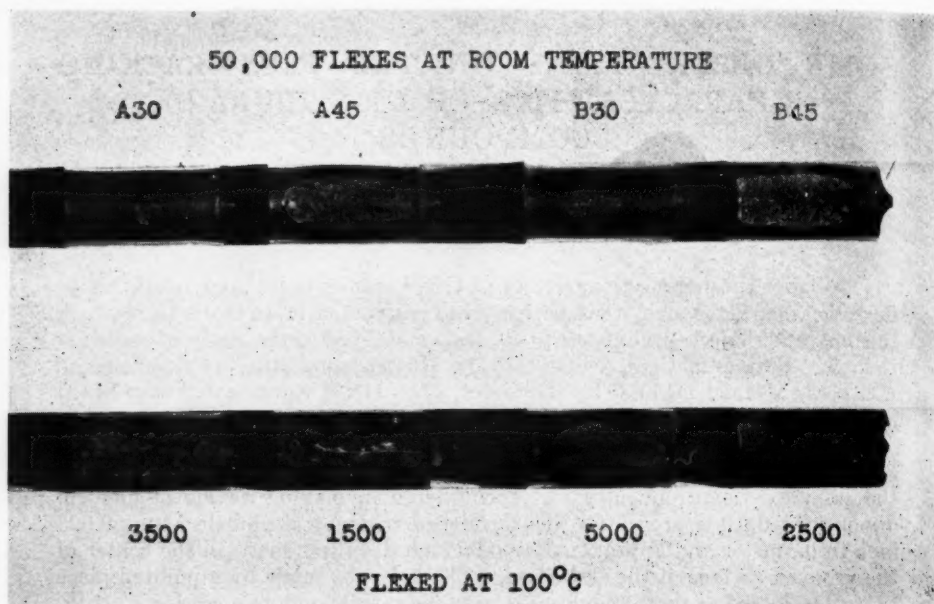


FIG. 1.

TABLE I (See Figure 9)

	A	B	C	D	E
GR-S	100.	100.	100.	100.	100.
Sulfur	1.5	1.5	1.5	1.5	1.5
Channel black (E.P.)	40.	40.	40.	50.	45.
Stearic acid	1.	1.	1.	1.	1.
Benzothiazyl disulfide	0.8	0.8	0.8	0.8	0.8
Litharge	1.2	1.2	1.2	1.2	1.2
Zinc oxide	5.	5.	5.	5.	5.
Bardol B	5.	5.	5.	5.	5.
Clay	—	15.	20.	—	10.
<i>Cure @ 287° F</i>	<i>Tensile—Lbs. Per Sq. In.</i>				
20 mins.	1910	1650	1600	1890	—
30 mins.	2130	2220	2200	2620	—
45 mins.	2670	2480	2390	2750	—
60 mins.	2670	2780	2550	2970	2760
75 mins.	2840	2660	2530	3030	—
120 mins.	—	2960	—	—	—
	<i>% Elongation</i>				
20 mins.	840	810	810	725	—
30 mins.	675	735	725	650	—
45 mins.	680	685	665	600	—
60 mins.	635	700	640	580	625
75 mins.	625	635	630	585	—
120 mins.	—	600	—	—	—
	<i>Modulus @ 300% Elongation</i>				
20 mins.	325	345	335	475	—
30 mins.	535	510	535	810	—
45 mins.	665	645	670	995	—
60 mins.	745	755	745	1100	835
75 mins.	790	800	760	1190	—
120 mins.	—	910	—	—	—

of "easy-processing" channel black and 10 volumes of titanium dioxide, in addition to vulcanizing agents and softener. Compound B is the same as A except that the titanium dioxide was eliminated and the channel black in-

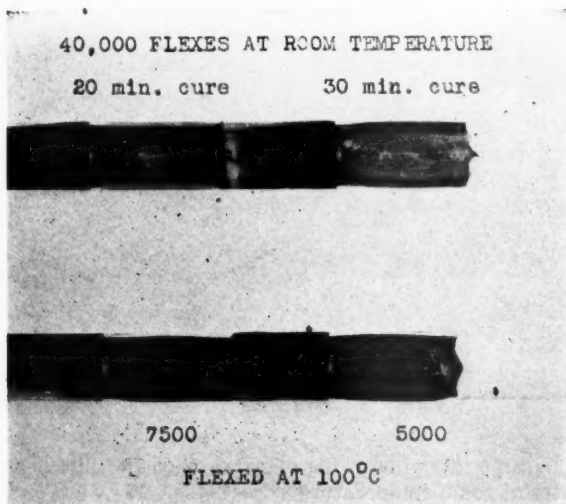


FIG. 2.

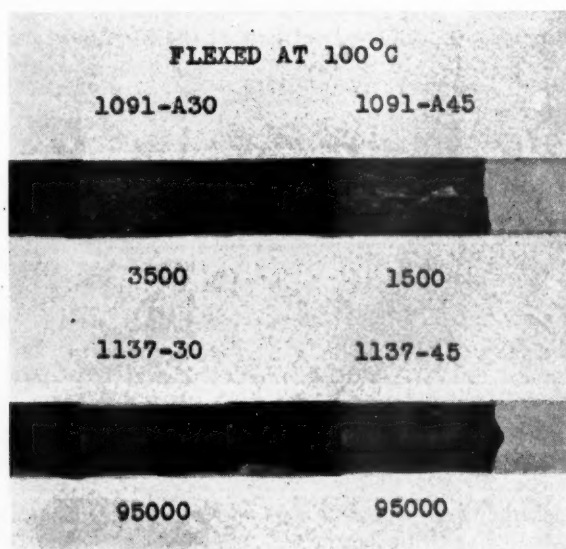


FIG. 3.

creased by 10 volumes. The increase in the cracking of each compound when flexed at room temperature as the cure is advanced from 30 to 45 minutes is

quite evident, as is the greatly accelerated rate of cracking when the flexing temperature is raised.

Figure 2 shows the effect of the state of cure and temperature of flexing on the cracking rate of a GR-S tread stock containing 50 parts of channel black.

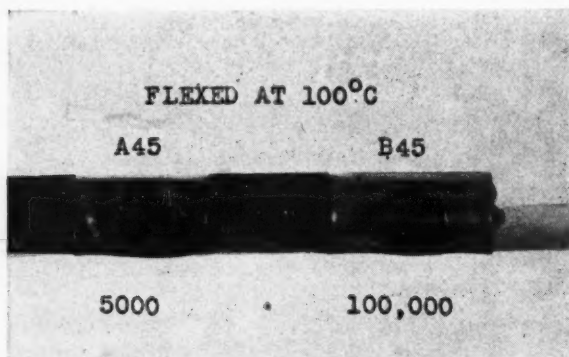


FIG. 4.

Here, again, the same rate of cracking is noted when the cure is advanced from 20 to 30 minutes at room temperature.

The improvement in flexing at 100° C induced by the addition of a small quantity of clay is illustrated in Figure 3. Compound 1091-A contains 15 parts of channel black and 10 volumes of titanium dioxide; Compound 1137 is an equivalent stock except that the titanium dioxide has been replaced with an equal volume of clay. It will be noted that, at the 30-minute cure, Compound

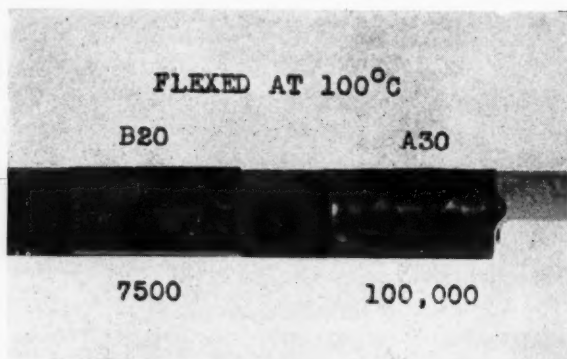


FIG. 5.

1091-A has cracked entirely across in 3,500 flexes, whereas Compound 1137 has cracked only about one-third as much in 95,000 flexes. The 1091-A sample has cracked almost completely through, while the crack in the other sample extends only as deep as the pin hole. Similarly, the 1137 stock is decidedly superior at the 45 minute cure.

Figure 4 represents a comparison between two GR-S tread stocks, Compound A containing 46 parts of channel black and B the same stock plus 10

volumes of clay. In fact, Compound B was formulated by adding clay to A. It will be seen that Compound B, when flexed 100,000 times at 100° C, has cracked less than one-half as much as Compound A flexed 5,000 times, thus bearing out the previous tests.

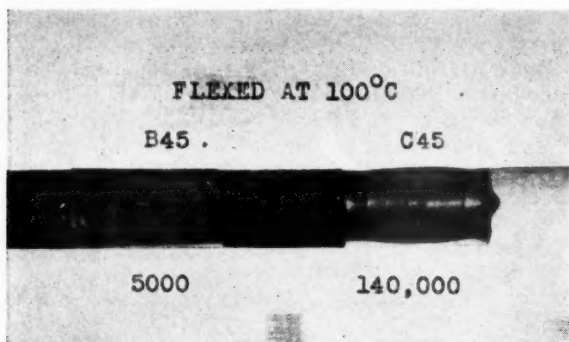


FIG. 6.

The increased hot flexing resistance imparted to GR-S carcass stocks by the addition of clay is again demonstrated in Figure 5. Here, Compound A contains 15 parts of channel black and 8 volumes of clay; B represents the same stock with the substitution of an equal amount of carbon black for the clay. It is seen that Compound A is in much better condition after 100,000 flexes at 100° C than Compound B in only 7,500 flexes at the same temperature.

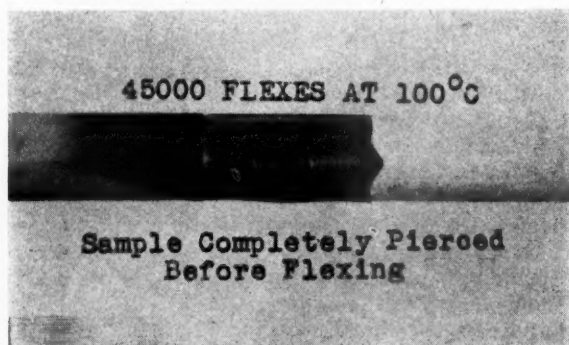


FIG. 7.

The same results are confirmed in Figure 6, in which Compound B contains 50 parts of channel black and C is the B stock plus 8 volumes of clay. Compound C has cracked far less in 140,000 flexes than B in only 5,000 flexes.

A slight variation in testing procedure was adopted in the case of Figure 7, the sample used containing 50 parts of channel black and 8 volumes of clay. Instead of the customary pinhole about 1/16 inch deep, the test-piece was completely pierced by a steel rod about 1/4 inch in diameter. The hole shows practically no increase in size after 45,000 flexes at 100° C.

The effect of increasing concentrations of clay on the hot flexing properties of GR-S carcass stock is well demonstrated in Figure 8. The compound contained 15 parts of channel black and, respectively, 2, 4, 6 and 8 volumes of clay. It will be noted that the compound containing only 2 volumes of clay cracked almost entirely across in only 2,500 flexes at 100° C; that containing 8 volumes of clay cracked only slightly at 100,000 flexes. A corresponding reduction in crack growth is very evident with increased loadings of clay.

Figure 9 shows the results on five GR-S tread stock samples, each containing different amounts of carbon black and clay. Specific formulas used and some physical test results are in Table I. It will be noted from Figure 9 that Compounds A and D have cracked almost entirely through in 5,000 flexes,

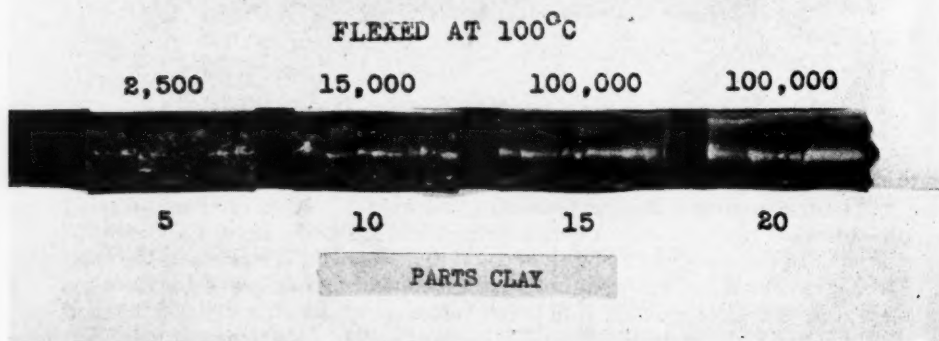


FIG. 8<sup>a</sup>

while the cracks in Compounds B and C are only about one-half as wide and much less in depth after 100,000 flexes. It will be seen also that Compound E in 25,000 flexes is in better shape than Compounds A and D in 5,000 flexes. Special note should be taken of the fact that, when cured for 120 minutes, Compound B cracked less severely in 60,000 flexes than Compounds A and D in 5,000 flexes at the 60-minute cure.

An indication that clay also imparts better flexing resistance to natural rubber treads is given in Figure 10, in which Compound A represents a 100% smoked sheet tread stock containing 40 parts of carbon black (with no antioxidant) and Compound B the same stock plus 6 volumes of clay. It can be seen that, when flexed at 100° C, the 15- and 30-minute cures of Compound A cracked much more severely than the corresponding cures of Compound B; in fact, Compound B at the 15 minute cure shows little cracking at 167,000 flexes.

The effect of clay on the hot flexing resistance of a natural-rubber tread stock, with and without clay, and a GR-S tread stock with 15 parts of clay is illustrated in Figure 11. Compound 1162-A is a 100% natural rubber tread stock containing 50 parts of channel black and antioxidant; 1162-B is the same stock, plus 6 volumes of clay; and 1158-B is a GR-S tread stock containing 40 parts of channel black and 6 volumes of clay. It will be noted that Compound 1162-B flexed much better than 1162-A at the 45- and 120-minute cures, and that the GR-S stock also flexed better than 1162-A at both cures. The

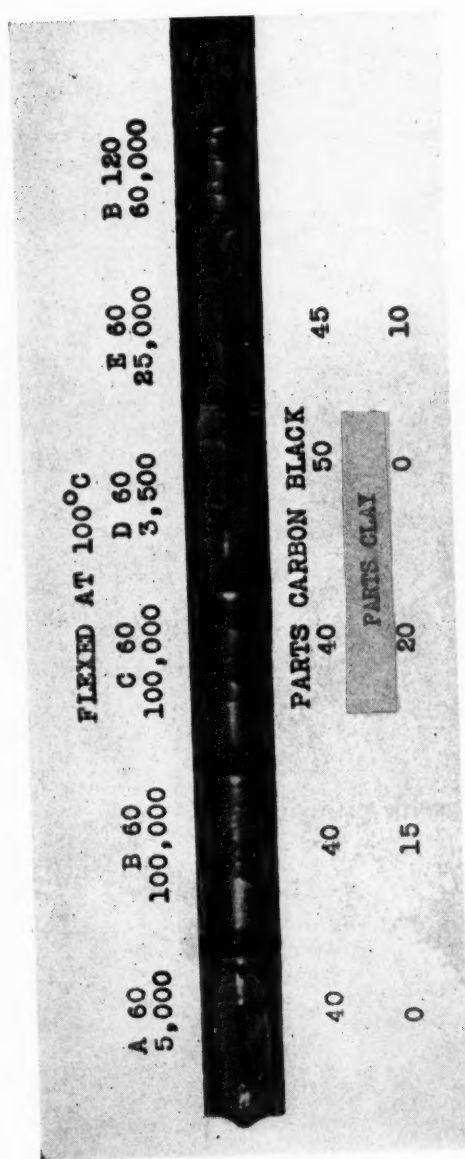


Fig. 9.



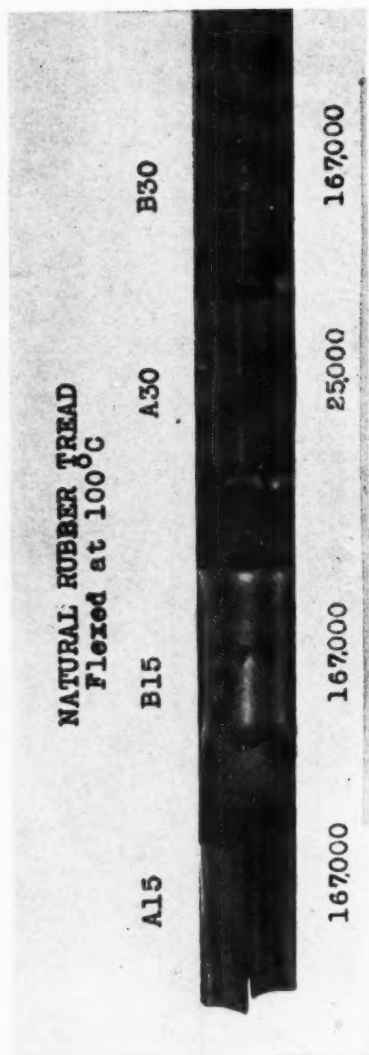


Fig. 10.

best performance was given by 1162-B (the natural-rubber stock with 15 parts of clay) at both the 45- and 120-minute cures, only slight cracking being evident at the 45-minute cure.

Judging from the appearance of the cracks, the manner in which they develop and the structure of the pigment itself it would appear that there is a definite orientation of the pigment which produces a laminated structure within the rubbers. An x-ray picture appears to confirm this supposition. The results aroused speculation regarding the practical value of this development, and preliminary tests were made to determine their performance in tires.

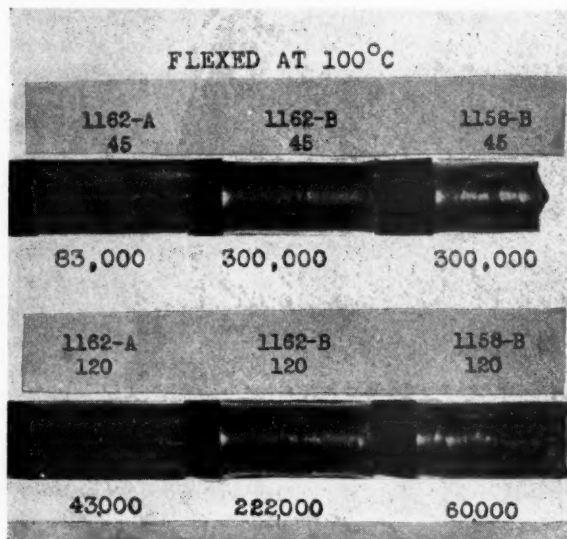


FIG. 11

A tire was fabricated with a composite tread; one-half a normal GR-S tread compound containing 40 parts of channel black; the other half identical except for the addition of 10 parts of clay. The tire was punctured by a sharp instrument entirely through the tread and carcass in several places, and a run was made on the test wheel. After completion of the run, an examination disclosed that several cracks proceeding from the punctures had developed in the normal tread stock but none in the special compound.

#### ACKNOWLEDGMENTS

The author is indebted to A. R. Kemp and W. O. Baker of the Bell Telephone Laboratories for the x-ray study. He is grateful also to O. J. Lang of the Armstrong Rubber Company for the manufacture and the testing of the experimental tire.

## EFFECT OF PETROLEUM PRODUCTS ON BUNA-S VULCANIZATES\*

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Little information has been published concerning the solvent or oil resistance of Buna-S. Street and Ebert<sup>1</sup> compared the swelling of stocks prepared from *Hevea* rubber, Buna-S, Buna-N, Neoprene, and Thiokol in gasoline, benzene, two lubricating oils, and water. They found that a Buna-S stock swelled approximately 60 per cent as much as a *Hevea* rubber stock in the gasoline and the two oils. Both Buna-S and *Hevea* stocks swelled much more than the Buna-N, Neoprene, or Thiokol stocks in these solvents.

The lack of interest in the oil and solvent resistance of Buna-S is due to the fact that it is not intended for use where liquid hydrocarbons come into contact with it. Nevertheless, in certain applications Buna-S may have casual contact with gasoline or oils—for example, in tire treads, conveyor and drive belt covers, hose covers, and wire insulation. On the basis of the previous information<sup>1</sup>, it would be expected that Buna-S would stand up as well as, if not better than, *Hevea* rubber in casual contact with gasoline or oils. Unfortunately this is not the case.

The authors first observed the peculiar effect of hydrocarbon solvents on Buna-S stocks while attempting to work out a method for repairing flaws in moulded articles. When a solvent or a cement of the stock was applied to the surface of the cavity to be filled, the article would break completely through if flexed even slightly before the solvent or cement had dried. Such a phe-

TABLE I  
RECIPES AND CURES FOR STOCKS TESTED

	<i>Hevea</i> pure gum	<i>Hevea</i> tread	Buna-S tread	Butyl tread	Neoprene- GN tread	Hycar OR-15 tread
Rubber	100.0	100.0	100.0	100.0	100.0	100.0
Channel black	...	50.0	60.0	50.0	35.0	50.0
Zinc oxide	3.0	3.0	5.0	5.0	5.0	5.0
Extra-light calcined magnesia	...	...	...	...	4.0	...
Stearic acid	1.0	3.0	2.0	3.0	0.5	1.5
Pine tar	...	3.0	...	...	...	...
Barrett No. 10 oil	...	...	...	...	5.0	...
Dibutyl phthalate	...	...	...	...	...	15.0
Cumar P25	...	...	...	...	...	10.0
Naftolen R100	...	...	5.0	...	...	...
Phenyl- $\alpha$ -naphthylamine	1.0	1.0	1.0	...	2.0	...
Phenyl- $\beta$ -naphthylamine	...	...	...	...	...	1.5
Mercaptobenzothiazole	1.0	1.35	...	0.5	...	...
Cyclohexylbenzothiazyl sulfamine	...	...	...	...	...	1.25
Tetramethylthiuram disulfide	...	...	...	1.0	...	...
Tetramethylthiuram monosulfide	...	...	0.5	...	...	...
Sulfur	2.75	2.75	2.0	1.5	...	1.25
Curing conditions						
Time (min.)	45	70	60	90	60	40
Temperature (° F)	260	260	260	307	274	307

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 35, No. 6, pages 646-649, June 1943.

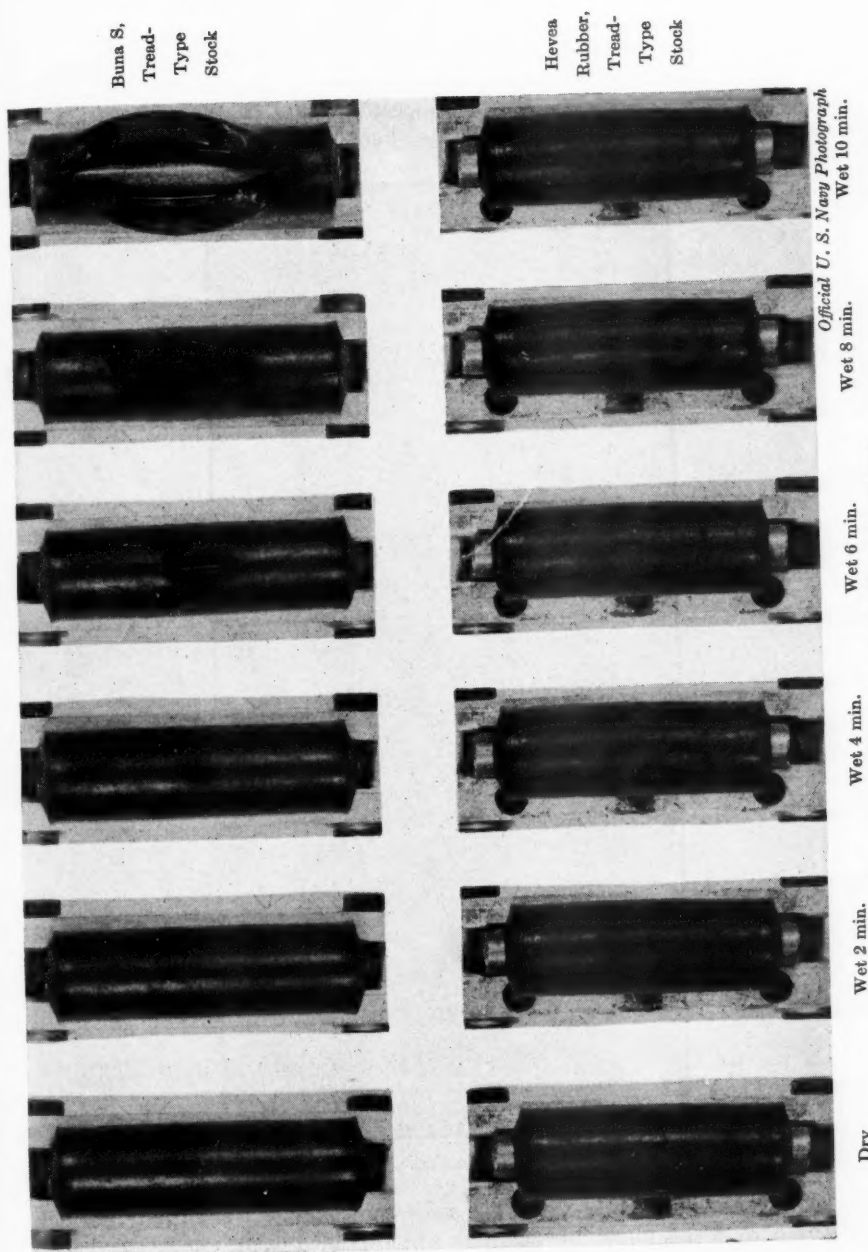


Fig. 1.—Effect of kerosene on cracks in bent specimens.

nomenon had never been observed in the case of other rubbers, either natural or synthetic.

#### LABORATORY INVESTIGATION

A rather crude but informative experiment was performed which demonstrated the poor tear resistance of a Buna-S vulcanizate when wet with kerosene. Slabs of a Buna-S and a *Hevea* tread stock (Table I), each  $\frac{1}{4}$  inch thick

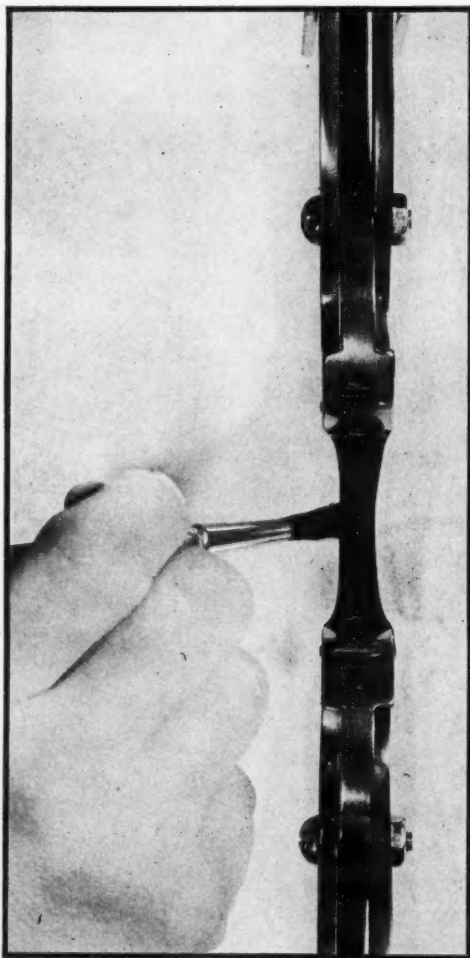


FIG. 2.—Method of wetting tear specimens with liquid petroleum products.

and  $2\frac{1}{4}$  inches wide, were cured. The slabs were clamped tight around  $\frac{3}{8}$ -inch o.d. tubing. A slit, about  $\frac{1}{4}$  inch long and  $\frac{1}{32}$  inch deep, was cut crosswise on the outer periphery of the curved slabs. Kerosene was painted onto the slits with a soft hand brush. The rate of growth of the slits was timed with a stop watch. The slit in the Buna-S stock soon cut through and, within 10

minutes, traveled almost the full width of the slab; the slit in the *Hevea* stock increased little in depth during this time (Figure 1).

Similar experiments on other Buna-S stocks gave the same results.

**Quantitative Measurement.**—The conventional laboratory test which comes closest to duplicating the flexing action responsible for the break described above is the A.S.T.M. test for tear resistance<sup>2</sup>. Accordingly, the effects of liquid petroleum products on the resistance to tearing of a Buna-S tire-tread stock were determined using A.S.T.M. type A specimens. A pure-gum *Hevea* stock and tire-tread stocks prepared from *Hevea* rubber, Hycar OR-15, Neoprene-GN, and Butyl rubber (Table I) were tested in a similar manner for comparison.

Tear resistances were first determined by the regular A.S.T.M. procedure. Then this test was repeated, except that a small brush, soaked with gasoline, kerosene, or turbine oil, was held lightly against the nick in the specimen (Figure 2) from the moment it was straightened by the machine grips until it broke. The characteristics of the gasoline, kerosene, and turbine oil are given in Table II; the results of these tests are presented in Figure 3.

TABLE II  
CHARACTERISTICS OF PETROLEUM PRODUCTS

	Aniline Point (° C)	Density at 60° F	Viscosity at 100° F (Saybolt Universal Sec.)
Gasoline	54.0	0.729	29
Kerosene	68.8	0.800	33
Turbine oil	84.7	0.922	495

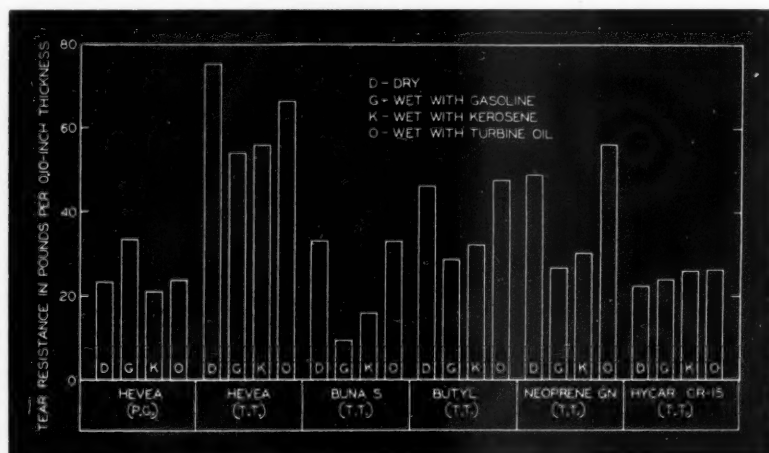


FIG. 3.—Effect of petroleum products on tear resistance at pulling speed of 20 inches per minute.

The plotted data indicate the severe action of gasoline and kerosene on the tear resistance of tread-type stocks prepared from *Hevea*, Buna-S, Butyl, and Neoprene-GN. Although the decrease in tear resistance of the Buna-S stock on a numerical basis was hardly any greater than that of the other stocks, the actual value of the tear resistance of the Buna-S stock in the presence of gasoline or kerosene was very low. The application of gasoline actually enhanced the tear resistance of the pure-gum *Hevea* stock. The tear resistance of the Hycar



OR-15 stock was little affected by gasoline or kerosene. The tear resistance of none of the stocks was changed to a significant extent by the turbine oil.

The small effect of turbine oil on tear resistance may be ascribed to its high viscosity. It would be reasonable to assume that, if the turbine oil were permitted to act on the specimens for a longer time, the tear resistance would suffer a greater decrease. This was proved to be the case, at least for the Buna-S and Neoprene-GN tread-type stocks, by repeating the tear resistance test at a pulling speed of 2 inches instead of 20 inches per minute (Figure 4).

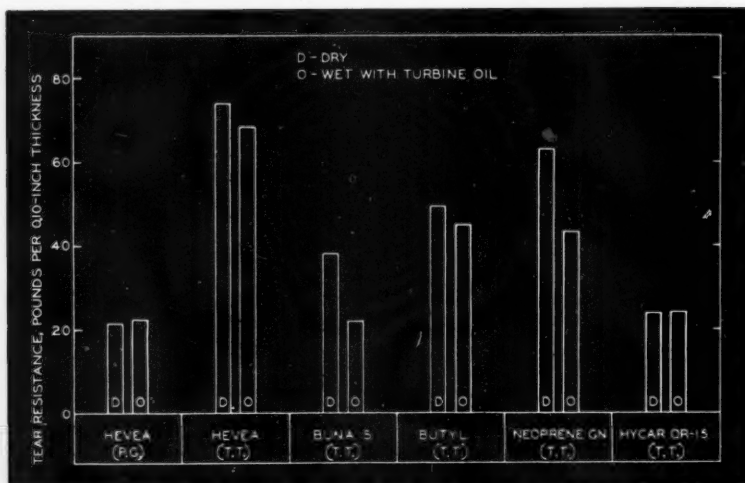


Fig. 4.—Effect of turbine oil on tear resistance at pulling speed of 2 inches per minute.

#### UNRELIABILITY OF USUAL TESTS

The severe effect of petroleum products on the tear resistance of Buna-S vulcanizates could not have been foretold from the results of ordinary swelling and tensile strength measurements after immersion. The rates of swelling in kerosene at 82° F of five stocks by the Garvey method<sup>3</sup> are given in Figure 5. They indicate that the Buna-S stock does not swell faster than the *Hevea* or Butyl stock.

The effect of 2-hour immersion in kerosene at 82° F on the tensile strengths of the vulcanizates is shown in Figure 6. These measurements were made according to the A.S.T.M. test for Immediate Deteriorated Properties<sup>4</sup>. The Buna-S stock had about the same tensile strength after immersion as the *Hevea* and Butyl stocks.

#### TESTS WITH THIN SPECIMENS

The authors believe that the inability of the swelling and tensile strength measurements, after immersion, to indicate the poor resistance of Buna-S vulcanizates to petroleum products may be due to the low rate of diffusion of these products into the Buna-S vulcanizates. Inasmuch as tearing starts at the surface, the lighter petroleum products would be expected to have almost an immediate effect on tear resistance. On the other hand, swelling and tensile strength are governed not only by surface conditions but also by those

in the interior of the specimens. Therefore, if a liquid is to have the same effect on swelling and tensile strength as it has on tear resistance, the liquid must diffuse rapidly into the rubber.

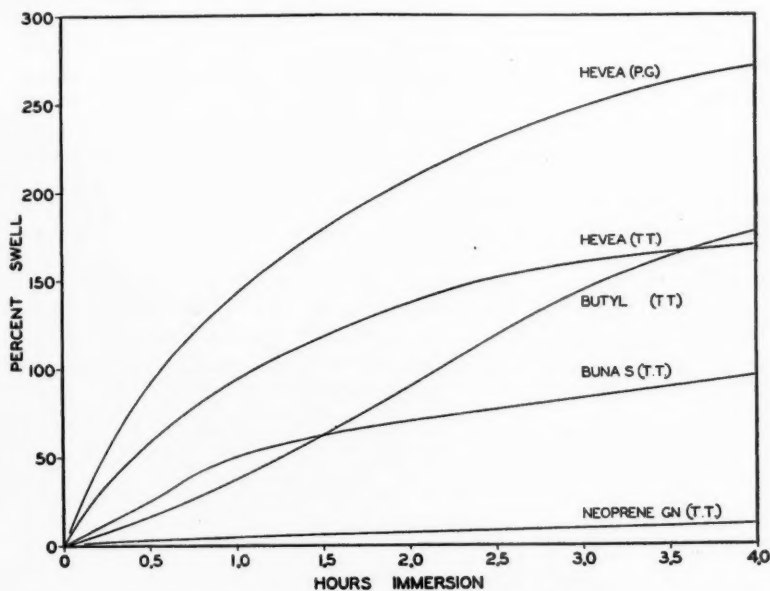


FIG. 5.—Rates of swelling in kerosene at 82° F.

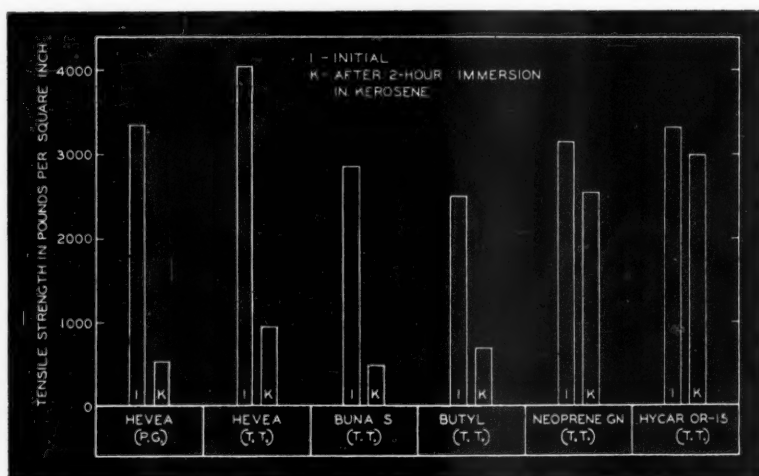


FIG. 6.—Effect of immersion in kerosene at 82° F on tensile strength.

To demonstrate the effect of kerosene on tensile strength when rate of diffusion is less of a factor, experiments were performed on samples 0.125–0.150 mm. thick. These paper-thin specimens were cut with the A.S.T.M. type C

die<sup>5</sup> from sheets which had been vulcanized between layers of cellophane in a hydraulic press. The specimens were secured at one end by a fixed clamp and stretched vertically to a given elongation by a suitable hanging weight attached to the other end. Kerosene was applied to the constricted portion by a soft brush. The time required for the sample to break after application of the kerosene was measured with a stop watch. If the specimen did not break within 15 minutes, more kerosene was applied every 15 minutes until breaking occurred.

Experiments were performed at 200 and 400 per cent elongation. Stretching the tensile specimens served two purposes: (1) it caused the specimens to become still thinner (*i.e.*, 0.040–0.052 mm. at 200 per cent elongation and 0.025–0.030 mm. at 400 per cent) and (2) it afforded a readily discernible end-point for deterioration.

Ten specimens of each stock were tested at each elongation. In addition, ten specimens of a Buna-S stock containing 40 parts channel black and ten specimens containing 20 parts channel black were tested at each elongation. These latter stocks were otherwise compounded the same as the Buna-S stock, which contained 60 parts of channel black. The stocks with lower loadings were included to illustrate the effect of modulus on this test.

During the tests, the specimens actually failed by tearing in the constricted portion instead of by a clean break, as in the ordinary tensile test. In every instance tearing was rapid after it started. The breaking times and the moduli of the stocks, determined with A.S.T.M. type C specimens, are listed in Table III. Each breaking time is the weighted average of ten determinations.

TABLE III  
EFFECT OF KEROSENE ON STRENGTH OF STRETCHED TENSILE SPECIMENS

Vulcanizate	Modulus of A. S. T. M. type C specimens (lb. per sq. in.)		Time to break thin specimens (min.)	
	At 200%	At 400%	At 200%	At 400%
Hevea (pure gum)	110	270	222.	0.62
Hevea (tread type)	530	1720	0.79	0.21
Buna-S with:				
20 parts black	190	500	0.22	"
40 parts black	310	1070	0.09	0.02
60 parts black	870	2410	0.06	0.01
Butyl (tread type)	190	650	1.04	0.43
Neoprene-GN (tread type)	830	2050	2.63	0.22
Hycar OR-15 (tread type)	510	1860	>840.0	0.77

" Time too short to measure accurately.

These results demonstrate even more strikingly than those of the conventional tearing test the exceptionally poor resistance of Buna-S vulcanizates to kerosene. The times required to break the stretched Buna-S specimens were generally an inverse function of the moduli of the respective stocks; but even the Buna-S stock with the lowest moduli had much shorter breaking times than the other rubbers. The very short breaking time of the Buna-S vulcanizate containing 20 parts of channel black at 400 per cent elongation may be attributed to the fact that its ultimate elongation before the application of kerosene was only 430 per cent.

Table III also shows that the *Hevea* pure gum specimens withstood kerosene much better than any of the tread samples except those prepared from Hycar OR-15. The relative ratings of the stocks for resistance to kerosene are

qualitatively the same at 200 and 400 per cent elongation, except in the case of the softest Buna-S and the Neoprene-GN. The latter stocks exhibited comparatively poorer resistance at 300 than at 200 per cent elongation.

### CONCLUSION

The authors believe that the tear resistance data presented in this paper should be kept in mind by anyone contemplating the use of Buna-S in applications where occasional contact with petroleum products may occur. The coincidence of the following three conditions on the surface of a Buna-S vulcanizate will almost certainly lead to a serious tear:

1. Cracking (weather cracks, cuts, gouges, snags).
2. Wetting with petroleum products, particularly the lighter variety.
3. Flexing, static or dynamic.

The tear will probably continue through the object until the flexing stress is relieved or until a fabric insert is reached. Thus, a tire tread would be torn through to the breaker fabric.

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# CONDUCTIVITY OF RUBBER TREAD STOCKS

## EFFECT OF PROPERTIES OF CARBON BLACK\*

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Considerable interest has been shown in semiconducting rubber compounds. These compounds are particularly useful where it is desirable to have a conducting path for the dissipation of static electricity. Examples of such application are shoe soles and flooring in certain plants, bus and automobile tires, etc. Semiconducting rubber can be prepared by the addition to the rubber formula of certain carbon blacks manufactured both from natural gas and acetylene. Unloaded rubber or rubber loaded with pigments other than carbon blacks has a specific resistance of  $10^{12}$  to  $10^{16}$  ohm-cm. By the addition of proper types of carbon black, resistances as low as 30–500 ohm-cm. can be readily obtained.

Several publications<sup>1</sup> have reported the effect of different carbon blacks on the conductivity of rubber stocks. In the present work an effort has been made to determine the influence of various fundamental properties of carbon black on the conductivity of a typical rubber tread stock test-formula. The properties considered are ultimate particle size, crystal form, and surface structure.

### PROCEDURE AND APPARATUS

The blacks were milled into the following standard tread formula:

Smoked sheet	100.	Sulfur	2.81
Zinc oxide	7.85	Captax (mercapto- benzothiazole)	0.743
Pine tar	3.00	Carbon black	50.5
Stearic acid	3.30		

Tensile sheets were cured at 280° F; a soap solution was used for mould lubrication, and reasonable care was exerted in curing and handling to prevent defacing the surface of the sheets. Resistance measurements were made before tensile strips were cut and broken. The specific resistance,  $R_s$ , listed for each black was taken on a tensile sheet cured at or near the cure giving the maximum tensile value. Resistance was determined by placing the tensile sheet between brass electrodes and measuring the current  $I$  and voltage  $E$ . All measurements were made at about 15 volts. Specific resistance  $R_s$  was calculated from the formula:

$$R_s = \frac{E}{I} \times \frac{31.6}{t}$$

where  $t$  = thickness of the rubber sheet (cm.)

31.6 = area of the electrode (sq. cm.)

An apparatus previously described<sup>2</sup>, and equipped with a device for applying sustained pressure, was used. The measurements were made under pressure to duplicate as far as possible the conditions under which a tire tread actually operates. Within the range of pressures used, a limiting value was reached, beyond which increasing the pressure decreased the resistance very

\* Reprinted from *Industrial & Engineering Chemistry*, Vol. 35, No. 7, pages 806–808, July 1943.

little; a constant pressure of 36 pounds per square inch was used, which was well above this limiting value. The average deviation of measured resistance for a given black run in the standard formula under standard conditions was found to be 25 per cent.

The degree of dispersion of carbon black in a rubber compound has been shown by other investigators to effect conductivity<sup>3</sup>. However, tests such as tensile strength before and after aging, hardness, resilience, and abrasion resistance, indicated that, for the stocks reported here, the degree of dispersion was very similar and could, therefore, have only a negligible influence on the general trends.

#### EFFECT OF PARTICLE SIZE

Table I gives the effect of particle size of carbon black on the conductivity of the rubber stock. Since the color of a rub-up of carbon black in oil varies

TABLE I  
EFFECT OF PARTICLE SIZE ON CHANNEL BLACK ON RESISTIVITY

Black	Estd. particle diam., $\mu$	Color	Volatile matter, %	$R_s$ , ohm-cm.
Continental AA	33	60	5.5	$7 \times 10^6$
Continental E	25	80	5.7	$5 \times 10^6$
Continental G	20	98	5.4	$3 \times 10^4$
Low-color	17	127	6.0	$6 \times 10^3$
High-color (Continex)	10	222	4.7	$2 \times 10^2$

principally with particle size, the color index as given in Table I is taken as a rough measure of surface area per unit weight. Also included in the table

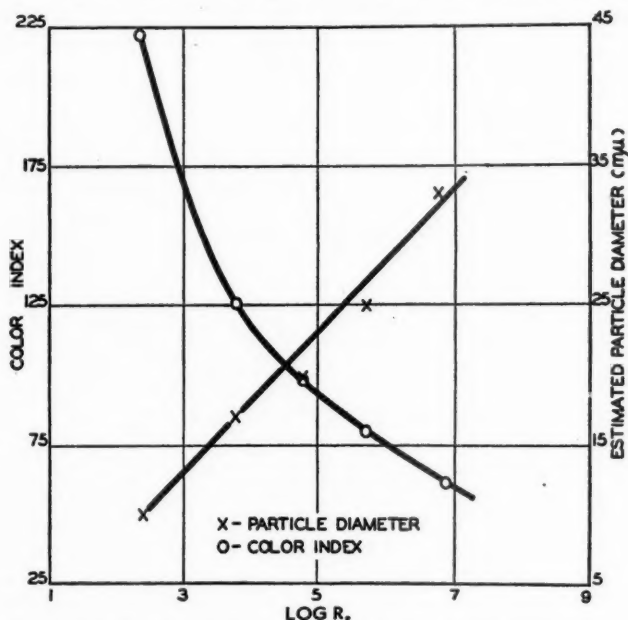


Fig. 1.—Effect of particle size and color index on specific resistance.



are estimates of actual particle diameters made from published electron microscope<sup>4</sup> and adsorption<sup>5</sup> measurements on similar blacks. In Figure 1 the logarithm of  $R_s$  is plotted against color index and estimated particle size.

As Table I shows, the specific resistance of a rubber stock varies exponentially with the diameter of the ultimate particles of carbon black used; these are channel blacks prepared from almost identical gases and permit the reasonable assumption that their crystal structure is very similar. The volatile content is a measure of the amount of volatilizable surface components of the black, and is sufficiently constant to have little influence on conductivity.

Kemp and Hermann<sup>6</sup> and Habgood and Waring<sup>7</sup> stated that the conductivity of rubber loaded with carbon probably occurs through chains of carbon particles which act as leakage paths for the current. As the particle size decreases, the number of particles in a given weight increases, and the probability of the formation of carbon chains increases enormously. The results of Table I are in full agreement with these considerations.

#### EFFECT OF CRYSTAL STRUCTURE

Blacks listed in series 1, Table II, have similar particle size and fairly similar volatile content but different crystal structures. Continental-AA is a

TABLE II  
EFFECT OF CRYSTAL STRUCTURE OF CARBON BLACKS ON RESISTIVITY

Black	Estd. particle diam., m $\mu$	Volatile matter, %	$R_s$ , ohm-cm.
Series 1			
Continental AA (devolatilized)	33	1.0	$8 \times 10^5$
Statex	34 <sup>a</sup>	0.8	$2 \times 10^5$
Graphon	33 <sup>b</sup>	0.4	$5 \times 10^2$
Shawinigan acetylene black	43 <sup>a</sup>	0.9	$1 \times 10^2$
Series 2			
P-33	74 <sup>a</sup>	0.5	$2 \times 10^{10}$
Gastex	81 <sup>a</sup>	0.2	$2 \times 10^8$
Lampblack devolatilized	97 <sup>a</sup>	0.6	$7 \times 10^4$

<sup>a</sup> Values were determined with the electron microscope by Wiegand and Ladd.<sup>4</sup> Smith, Thornhill, and Bray<sup>5</sup> give the following particle diameters as calculated from adsorption measurements: Gastex = 75 m $\mu$ , lampblack = 107 m $\mu$ , P-33 = 200 m $\mu$ .

commercial channel black prepared from natural gas. Materials of this type give an x-ray pattern with diffuse bands. Graphon is prepared by heating channel black for several hours at about 2000° C.<sup>8</sup> As a result of this treatment, the x-ray pattern becomes much sharper and more nearly approximates that of graphite<sup>9</sup>; the conductivity as indicated in Table II is markedly increased. Shawinigan black is made by the thermal decomposition of acetylene gas, and the higher temperature prevailing during formation of this black makes it probable that a greater extent of crystal growth occurs. The results of heat of combustion determinations indicate that acetylene black is closer to graphite than channel black<sup>10</sup>. Likewise, x-ray photographs indicate a more nearly graphitic structure for acetylene black than for ordinary channel black<sup>11</sup>. However, Biscoe and Warren<sup>9</sup> indicated that when heated at high temperature, channel black, as in the case of Graphon, increases in crystal dimensions and becomes similar to acetylene black.

The position of acetylene black in Table II is in qualitative agreement with these considerations; however, in comparison with Graphon, acetylene black

is slightly better conducting than might be expected considering the x-ray data of Biscoe and Warren<sup>9</sup> and the particle size estimates of Table II. Statex is prepared by partial combustion at rather high temperatures.

A second series of blacks of similar particle size and volatile content appears in Table II. Owing to the different production conditions (P-33 by thermal decomposition of natural gas diluted with hydrogen, Gastex by partial combustion of natural gas and lampblack by partial combustion of higher hydrocarbons), we would again expect differences in crystal structure among the products.

Both lampblack and acetylene black were reported to differ from other blacks in their appearance under the electron microscope<sup>12</sup>. Ultimate particles of lampblack and acetylene black group together as irregular networks in the specimens prepared for examination with the electron microscope, whereas other blacks, such as ordinary channel black, Statex, Gastex, and P-33, appear either as individual particles or flocs. These tendencies are probably due to crystal structure factors which distinguish acetylene black and lampblack from the other blacks. The conductivity values in Series 2, Table II, show that, like acetylene black, lampblack has a higher conductivity than other carbons of similar diameter and volatile content.

#### EFFECT OF SURFACE STRUCTURE

The samples listed in Table III were prepared by partially removing the volatilizable surface components from a moderately small particle size (17 m $\mu$ ) channel black (Continental C-15).

TABLE III  
EFFECT OF SURFACE STRUCTURE OF CARBON BLACKS ON RESISTIVITY

Medium-color black	Volatile matter <sup>13</sup> (Percentage)	Diphenylguanidine <sup>14</sup> (Percentage)	% I <sub>2</sub> *	R <sub>s</sub> , ohm-cm.
Original	4.3	56	62	5000
Partly devolatilized	3.3	36	65	3500
Partly devolatilized	1.8	23	70	3300
Partly devolatilized	1.2	12	75	1100
Completely devolatilized	<0.15	4	73	400

\* Adsorbed by 1 gram black (to which 10 cc. 10% H<sub>2</sub>SO<sub>4</sub> has been added) from 100 cc. of I<sub>2</sub> solution in KI containing 2.7 grams I<sub>2</sub> and 4.05 grams KI per liter of solution.

The volatile matter was reduced by heating the black for various periods in a nonoxidizing atmosphere. Since the temperature in all cases was kept below 800° C, no significant change in either particle size or crystal structure could have occurred. Hence the differences in conductivity can be attributed solely to the surface structure of the blacks. The conductivity increases appreciably as the volatile content decreases (Figure 2). The per cent diphenylguanidine is a measure of the amount of oxygen-containing complexes present on the surface of the black. Figure 2 shows that there is even closer correspondence between per cent diphenylguanidine and conductivity than between volatile content and conductivity. The iodine adsorption corresponds roughly to the bare carbon surface. As the volatile content is removed, the extent of carbon surface is increased, and the per cent iodine adsorbed is also increased. The iodine adsorption of the completely devolatilized sample is lower than would be expected, owing possibly to the higher temperature of devolatilization.

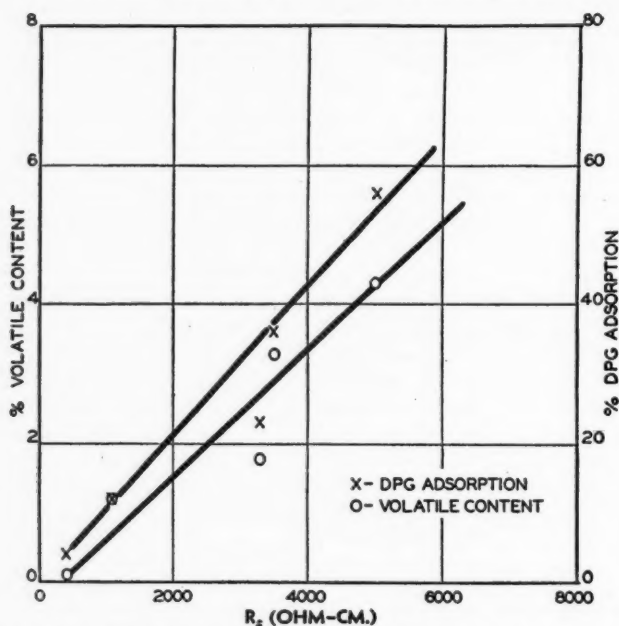


Fig. 2.—Relation of specific resistance to DPG adsorption and volatile content.

The influence of volatile matter content is further illustrated in Table IV.

TABLE IV  
EFFECT OF CHANGING VOLATILE CONTENT OF STANDARD  
RUBBER-GRADE CHANNEL BLACK

Continental E Black (25 $\mu$ )	Volatile matter (%)	Diphenyl- guanidine (%)	Iodine $I_2$ (%)	$R_s$ , (ohm-cm.)	Resistance of un- compounded black, (ohm-cm.)
1. Volatile increased	9.7	86	28	$4 \times 10^6$	5000
2. Untreated	5.7	50	44	$5 \times 10^5$	2500
3. Volatile decreased	1.8	12	72	$1 \times 10^5$	750

Sample 2 was the untreated black, sample 3 was the same black with the volatile partially removed, and sample 1 was prepared by treating sample 2 in an oxidizing atmosphere to increase the oxides present on the surface. The results are in complete agreement with those of Table III. Also shown in Table IV is the effect of changes in volatile content on the conductivity of the uncompounded carbon black. This type of measurement depends on physical factors, such as the size of pellets or aggregates present in the black and the degree of packing of these aggregates, so the results are only of relative importance.

The conductivity of a commercial lampblack (estimated particle diameter 97  $\mu$ ) before and after the volatilizable surface components had been removed is shown in Table V. As indicated by the low diphenylguanidine adsorption, the volatile content of lampblack consists chiefly of hydrocarbons rather than oxides of carbon. In this case, also, removal of the surface film led to strikingly higher conductivity.

The foregoing indicates that noncarbon surface components on carbon blacks act as an electrically insulating layer. Since the electric current is

TABLE V  
RESULTS ON LAMPBLACK

Lampblack	Volatile matter (%)	Diphenylguanidine (%)	Iodine (%)	$R_s$ (ohm-cm.)
Original	4.5	21	16	$1 \times 10^7$
Devolatilized	0.6	5	28	$7 \times 10^4$

probably carried through rubber loaded with carbon black along conducting chains of the black, a nonconducting layer preventing good contact between the carbon black particles lowers the conductivity considerably. For example, in the case of the Continental-E series of Table IV, a surface layer 2.5 Å.U. thick on the carbon particle is roughly equivalent to a nonconducting film of 0.2 mm. on one side of a test-sheet 1 cm. thick. (A surface layer 2.5 Å.U. thick causes an insulating film of 5 Å.U. between carbon particles. Since, for Continental-E, the particle diameter is about 250 Å.U., the thickness of the insulating film is about 2 per cent of the total thickness. Ignoring variation in specific resistance with thickness, this would be equivalent to a 0.2-mm. film on a sheet 1 cm. thick.)

#### SUMMARY

The conductivity of a rubber tread stock compounded with 50 parts of carbon black increases exponentially as the particle size of the black decreases. As the crystal structure of the carbon approaches a more graphitic form, the conductivity increases sharply. Noncarbon surface components, either of the hydrocarbon or carbon oxide type, decrease the conductivity. This effect is less important than particle size or crystal structure. However, increases in conductivity or more than tenfold can be brought about by removal of surface components.

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## AGING OF RUBBER IN THE OXYGEN BOMB AT ROOM TEMPERATURE\*

J. R. SCOTT

The work described below was carried out as a first step in determining whether an oxygen-bomb test at room temperature could be used as an accelerated aging test for unvulcanized rubber compositions, *e.g.*, as used on surgical and adhesive plasters and for combining shoe fabrics, because a high-temperature test is unsatisfactory in such cases, owing to the melting of the compositions. The only infallible way of assessing the value of an accelerated test for such compositions is by comparison with natural aging, but as this is a very lengthy process and as the deterioration is difficult to measure quantitatively, it was decided to make preliminary tests on the effect of high oxygen concentration at room temperature by using vulcanized rubber.

Although the results proved to be negative so far as the original purpose of the work was concerned, it is considered of interest to place them on record in view of the prominence given in some papers on aging<sup>1</sup> to the relationship between oxygen concentration and rate of oxidation and deterioration of rubber.

A mix composed of rubber 100, sulfur 3, zinc oxide 5, stearic acid 1, and diphenylguanidine 0.75, was vulcanized for 30 minutes at 153° C. Tensile tests, using standard ring-specimens and the Schopper machine, were made on unaged specimens and on specimens that had been aged (1) in an oxygen bomb at 300 lb. per sq. in. oxygen pressure and at room temperature (about 10° C), (2) in a Geer oven at 70° C. Four rings were used for each test, the tensile strength and breaking elongation figures quoted being the average for the two rings giving the highest tensile strength, and the figures for the elongations at constant loads the average of all four rings.

Aging	Tensile strength (kg. per sq. cm.)	Breaking elongation (%)	Elongation (%) at load (kg. per sq. cm.) of:			
			25	50	75	100
Unaged	210	756	405	530	595	630
Bomb, 5 days	216	750	383	518	577	618
" 8 "	207	745	395	527	580	622
" 12 "	207	749	398	528	583	625
" 30 "	193	715	363	470	540	600
Oven 5 days	125	664	337	484	585	630
" 8 "	23	309	324	—	—	—

If tensile deterioration proceeded at a rate proportional to oxygen pressure, it would be 100 times as fast in the oxygen bomb as in air at normal pressure at the same temperature. Since the Geer oven test accelerates deterioration by 100–200 times, the rate of deterioration in the bomb at room temperature would thus be comparable with that in the Geer oven. This is clearly not so, deterioration being very much slower in the bomb, since only after 30 days are there definite signs of a fall in tensile strength, whereas 5 days in the oven produces serious deterioration.

These results agree with those of other workers, *e.g.*, Milligan and Shaw<sup>2</sup>, and Morgan and Naunton<sup>3</sup>, in showing that the rate of oxidation, and hence of

\* Reprinted from the *Journal of Rubber Research*, Vol. 12, No. 6, pages 47–48, June 1943.

tensile deterioration, does not increase anything like as rapidly as the oxygen concentration. According to Morgan and Naunton<sup>3</sup>, the explanation of this fact is that the oxidation is a chain reaction, and since this is true of both raw and vulcanized rubber, it would appear that a high-pressure oxygen test at room temperature would be no more effective as an accelerated aging test for unvulcanized rubber compositions than for vulcanized rubber.

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# NITROPARAFFINS IN THE RUBBER INDUSTRY\*

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A recent development in the field of industrial chemicals which has met with widespread interest is the first commercial production of nitroparaaffins in 1940. The announcement of nitroparaaffins to industry was followed by extensive investigations in industrial and research laboratories of the suitability of these compounds in a wide variety of applications, including many in the field of rubber technology. It is the purpose of this paper to summarize the more promising applications of the nitroparaaffins in the rubber industry which have so far been reported.

## APPLICATION AS RUBBER SOLVENTS

Among the first successful applications of nitroparaaffins was their use in solvent formulations. Extensive tests by the research department of Commercial Solvents Corporation and others showed that nitroparaaffins and their derivatives are solvents for many synthetic plastics, including important cellulose esters, vinyl resins, and some of the synthetic elastomers now being developed to replace natural rubber. In particular, the manufacturer of Hycar-OR reported<sup>1</sup> that this synthetic rubber dissolves readily in nitroparaaffins, and

TABLE 1

### SOLUBILITY OF VARIOUS SYNTHETICS IN NITROPARAFFINS

Key: E, Excellent solvent; G, Good solvent; SW, Swells the material under test; I, Insoluble; SA, Soluble in presence of alcohol

Synthetic	Nitro- methane	1-Nitro- propane	1-Chloro-1- nitropropane
<b>A. Hydrocarbon soluble</b>			
Buna-S	I	I	SW
Buna-N (Perbunan)	SW	E	E
Chemigum	SW	G	E
Neoprene-GN	I	SW	E
Neoprene-CG	I	SW	G
Butyl Rubber	I	I	I
Vistanex (medium)	I	I	I
Vistanex No. 6	I	I	I
<b>B. Hydrocarbon insoluble</b>			
Hycar-OR	E	E	E
Vynlite-XYSG	SW	SW	SW
Vynlite-QYNA	I	SW	SW
Koron-101	I	SW	G
Flamenol S-717	I	SW	SW
Flamenol S-720	I	SW	SW
Butacite			
Commercial grade	I	I	I
RH-410 M	I	G	E
RW-410	I	G	G
Cellulose acetate	G	SA	I
Cellulose acetobutyrate	G	E	E

\* Reprinted from the *India Rubber World*, Vol. 107, No. 2, pages 169-170, November 1942.

these solutions have proved valuable in cements and in coatings used for waterproofing fabrics. The solvent powers of two nitroparaffins and of a typical halonitroparaffin for a number of common synthetic plastics and elastomers are shown in Table 1.

### USES IN RUBBER CEMENTS

The use of accelerated rubber cements has been limited in the past because of their instability. Very often the cements gelled quickly after they were prepared; it was necessary, therefore, to formulate them as two separate solutions which could be mixed just before the cement was used. This procedure, besides being inconvenient, was very wasteful, since any unused cement quickly gelled and became worthless. For example, if a typical two-part cement of the following composition is mixed, it gells within a short time so it can no longer be used.

#### RECIPE 1

DISSOLVE IN BENZENE OR OTHER SUITABLE SOLVENT:

	Part A	Part B
Rubber	100	100
ZnO	10	
Sulfur	6	
Zinc dibutyldithiocarbamate		1
Polybutyraldehydeaniline		1
	116	102

However the addition of a quantity of 1-chloro-1-nitropropane equal to the weight of the rubber inhibits greatly the gelling time, and the use of the cement becomes much more convenient and economical. Thus this important objection to accelerated rubber cements may now be eliminated by the use of nitroparaffins and their derivatives as gelling inhibitors<sup>2</sup>.

The effectiveness of a typical nitroparaffin and of a typical halonitroparaffin in stabilizing a cement of 10 per cent rubber content made with various solvents is illustrated in Table 2. The nonvolatile portion of these cements was the same as that of the two-part cement described in Recipe 1.

TABLE 2  
NITROPARAFFINS AS STABILIZERS FOR RUBBER CEMENTS

Solvent	% Stabilizer by wt.	Benzene	Naphtha	Ethylene Dichloride
		Gelling Time at 50° C (hours)		
	None	33.5	144	87
1-nitro-2-methylpropane	1	39.5	132.5	96
1-nitro-2-methylpropane	5	54.0	118	111
1-nitro-2-methylpropane	10	57.5	108	>284*
1-chloro-1-nitropane	1	63.5	201	>284*
1-chloro-1-nitropropane	5	162	>411*	>284*
1-chloro-1-nitropropane	10	>421*	>411*	>284*

\* Not gelled when test was stopped.

The results given in Table 2 indicate that nitroparaffins retard gelling in benzene and ethylene dichloride cements, but promote gelling in naphtha cements. Halonitroparaffins, on the other hand, serve as antigelling agents in all three solvents.

These tests reported in Table 2 were run at 50° C to obtain quick results. These results, however, are not necessarily an indication of the stability of cements during storage under normal conditions. As a more practical test, samples of these cements were stored at 82° F, and after three years those containing 1-chloro-1-nitropropane were still fluid.

All of the foregoing tests were made on cements that contained no pigments. The effect of loading agents on the stability of cements containing 1-chloro-1-nitropropane was studied by aging a series of cements prepared by direct mill-mixing of Recipe 1, adding 100 parts by weight of the loading agent for each 100 parts by weight of rubber. With each pigment two cements were prepared: one with and one without 1-chloro-1-nitropropane, and all the cements were aged at 50° C. The results are given in Table 3.

TABLE 3  
STABILIZATION OF LOADED CEMENTS WITH 1-CHLORO-1-NITROPROPANE

Pigment	Gelling Time at 50° C	
	without 1-chloro-1-nitropropane (hrs.)	with 1-chloro-1-nitropropane (hrs.)
None	32	1224*
Whiting	31	1224
Magnesite	31	384
Lithopone	31	840
Titanium dioxide	22	1224

\* Not gelled when test was stopped.

Table 3 indicates that 1-chloro-1-nitropropane inhibits gelling satisfactorily in cements containing inert loading agents. Other experiments have shown, definitely, however, that strongly basic materials such as lime and magnesia destroy the inhibiting action of 1-chloro-1-nitropropane, probably because of salt formation, since the nitroparaffins can react as acids in the presence of alkaline materials. For the same reason, cements that are accelerated with diphenylguanidine (an alkaline compound) cannot be stabilized with 1-chloro-1-nitropropane.

Cements prepared from various butadiene rubbers have been stabilized satisfactorily with chloronitroparaffins. The results of comparative tests on three of the synthetics are given in Table 4.

TABLE 4  
STABILIZATION OF SYNTHETIC RUBBER CEMENTS BY 1-CHLORO-1-NITROPROPANE

Formula	(1)	(1-A)	(2)	(2-A)	(3)	(3-A)
Hycar-OR	100	100				
Perbunan			100	100		
Buna-S					100	100
Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5
Butyl Zimate	0.5	0.5	0.5	0.5	0.5	0.5
Polybutyraldehydeaniline	0.5	0.5	0.5	0.5	0.5	0.5
Cements made up to 20% rubber content	Methylisobutyl ketone		Benzene		Benzene	
1-Chloro-1-nitropropane used at 20% on the total cement	No antigel	Antigel added	No antigel	Antigel added	No antigel	Antigel added
Gelling time at 50° C (hrs.)	23	462*	29	388	42	388*

\* Not gelled when test was stopped.

In general, highly accelerated cements with excellent nongelling characteristics can be prepared from natural rubber, Hycar-OR, Perbunan, and Buna-S by inhibiting vulcanization through the use of 1-chloro-1-nitropropane or other nitroparaaffins. Such cements tend to have excellent bonding power, but the chloronitropropane causes somewhat slower curing, owing to retention of the antigel in the film.

#### HEAT SENSITIZATION OF LATICES

Experiments on rubber latices have shown that nitroparaaffins and their derivatives are very effective heat sensitizers for aqueous dispersions of rubber and rubber-like materials, both natural and synthetic<sup>3</sup>. The effects of a typical nitroparaaffin, a typical halonitroparaaffin, and a typical nitroalcohol on a natural rubber latex are given in Table 5.

TABLE 5  
NITROPARAFFINS AND DERIVATIVES AS HEAT SENSITIZERS<sup>4</sup>

Formula: 60% Hevea latex		167 g.	
ZnO dispersion		4 g.	
Heat sensitizer		2 g.	
		<hr/>	
		173 g.	
Temperature	28° C	50° C	80° C
	Gelling Time (hrs.)		
Blank	No gel	6.17	0.13
Nitroethane	24	0.22	0.07
1-Chloro-1-nitropropane	48	0.50	0.10
2-Nitro-2-methyl-1-propanol*	240	3.33	0.10

\* The nitroalcohol was added as a 10% aqueous solution to prevent local coagulation.

The tests reported in Table 5 disclose the interesting and unexpected fact that compositions sensitized with 2-nitro-2-methyl-1-propanol require a long time to gel at room temperature, but they are very sensitive to heat at 80° C. Further work has shown sensitized latices to remain unchanged during long storage at room temperature if a very stable latex is used in their preparation. Latices sensitized in this way may be used in any commercial process such as the manufacture of sponge rubber and of moulded and dipped goods where the use of heat for rapid establishment of the desired gel is permissible.

These uses for nitroparaaffins and their derivatives which have just been discussed only hint at their ultimate importance to the rubber industry. In addition to their direct uses, they give promise of proving even more useful as starting materials in formulating new accelerators, antioxidants, and other chemicals required by the expanding field of rubber chemistry—particularly in connection with synthetic rubber developments. The versatility of nitroparaaffins in synthesis will help rubber chemists in solving many of their perplexing problems.

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## BRASS-PLATING \*

W. A. GURNEY

Although brass-plating is the best known method of attaching rubber to iron or steel, it is still regarded in many quarters as something of an art or mystery, with a considerable element of uncertainty entering into the process.

The brass-plating bath consists essentially of copper and zinc cyanides dissolved in sodium or potassium cyanide, with a total metal content of about 3 ounces per gallon. The composition of the alloy deposited varies with the ratio of copper to zinc in the bath, the pH, the temperature, the current density, and the amount of certain other substances, such as ammonia. Most writers on the subject have endeavored to eliminate the uncertainty by a rigorous specification of the formula of the plating bath, and the conditions under which it is to be used.

In his experience, however, the composition of a plating bath can vary widely, and still give plating satisfactory for adhesion. The composition of plate deposited depends on a balance of several factors, and in most published formulas, one or more of these factors is omitted. For example, the pH is often not specified and yet it is possible to deposit a range of brasses from pure copper to pure zinc merely by the change in pH, in any particular bath.

The bath to be used is one that is stable in operation, and gives a brass containing approximately 70 per cent copper, 30 per cent zinc, and clean and free from adsorbed impurities. So long as these conditions are obtained, the exact composition of the plating bath is of little importance.

When the plater has obtained a brass of this type, he has a clean ideal surface to which the rubber can be bonded. The problem is now to preserve this surface. It is probably not appreciated how much the bonding owes to the freshly prepared clean surface. If such a surface could otherwise be obtained, many other bonding methods would give good results, probably equal to brass plate. In many cases they are not given a fair chance, because the metal parts have not had such a drastic cleaning.

The brass surface is surprisingly resistant to chemical treatment. The plated surface may be immersed in dilute acids or ammonia, used as electrode in electrolytic baths and even dipped in weak soap solution without harm. On the other hand, if as little as 0.5 mg. per sq. inch of sodium hydroxide or carbonate is allowed to dry on the surface, the adhesion is almost completely spoiled. This point is rather important, as it is suspected that such materials may be adsorbed on the brass surface if the washing water becomes alkaline, or if the pH of the plating bath is too high.

Fatty substances, such as used for protecting the workers hands, are harmful. Mineral oils, stearates and other substances soluble in rubber are not harmful to the bond, but may easily damage the rubber if present in excess. Such sources of contamination are fairly easily avoided, but there is one important cause of trouble that is generally overlooked. That cause is contamination during vulcanization.

A series of experiments was made to find the best curing conditions. Samples of rubber were calendered between cloth, so as to give the surface a

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pronounced cloth mark. Pieces of this rubber were moulded under light pressure for various times, and the cure completed under full hydraulic pressure. When the bonds were broken after cure, a perfect pattern of the cloth was marked in torn rubber on the surface of the brass. This seemed to show that the rubber had scorched, but further examination showed that the rubber had moulded out perfectly, and that the pattern on the brass was due to rubber torn out of the surface. The first parts of the rubber to touch the surface had stuck much more firmly than those moulding out later, and this will be found to be a general rule. Further experiments showed that brass plate discolored rapidly in the presence of hot rubber.

It is generally agreed that the brass plate unites with sulfur during the vulcanization process, and from these experiments, and others suggested by them it is concluded that the combination of copper and rubber with sulfur should occur simultaneously.

Partly vulcanized rubber or Neoprene adhere well to brass plate, because the combination with sulfur can continue so long as free sulfur exists, but the reaction of brass with sulfur does not seem to be continuous in this way. A few minutes at a high temperature are sufficient to contaminate the metal surface and give a poor bond.

The practical consequences of such a reaction are considerable. Translated into practice it means that the rubber must be brought intimately into contact with the plating and raised to a high temperature as quickly as possible. Long soaking periods before cure or slow rises are likely to be detrimental, and by experiment have been found to give inferior results.

This theory also explains the contradiction between the excellent bonds which can be obtained with quite light pressure and the high hydraulic pressures which are usually recommended for bonded articles. The high pressure is needed only to get the rubber into rapid contact with the plate, and if this can be obtained by other means, the results will be equally satisfactory.

It has also an important meaning for the mould designer. It is usual to vent complicated shapes to prevent bare moulding, but this becomes of even more importance for bonding. Air must be removed rapidly, and mould designs which tend to trap air give defective articles. The air may diffuse out or dissolve in the rubber, so that perfect moulding is obtained, but the bond will have been spoiled, and another article will have been unjustly condemned for faulty plating.

In this respect steam is as bad as air, and many metal articles are sufficiently microporous to retain traces of water from the plating process, which may cause local damage and a loss of strength in the bond. Such porosity may occur from overpickling, or during manufacture of the metal part.

This hypothesis that the early stages of cure are most important may explain the difficulties obtained with rubber flow. Bonds are often poor where excessive flow occurs, and yet many articles are made in which the rubber moves considerably in moulding. If the rubber moves and reaches its final position before curing commences, all will be well. Should, however, movement continue, due to thermal expansion of the body of the rubber or to other cause after curing has begun, the bond is likely to be torn apart and any bonding that occurs afterwards will be inferior.

This explains also the variation in effect found with different accelerators. If the union of copper and rubber with sulfur is to occur simultaneously, the acceleration of the compound should not be too fast, which favors the rubber,



or too slow, which allows contamination of the brass. A medium speed, general purpose accelerator will generally be found satisfactory.

If the brass plate has survived the many possible sources of contamination, the final bond will depend on the characteristics of the rubber bonded. Unloaded rubbers give low adhesions, and the bond increases as the compound is loaded. The strength of the bond seems to follow the reinforcement of the compound fairly closely. If different carbon blacks be compared, for example, it is found that the bond strength increases as the particle-size decreases, that is, in a similar way to the reinforcing properties. Again, it is often said that there is an optimum rubber hardness for bonding, and it is certainly found that hard rubbers tend to give variable results. This decrease in bond, however, occurs when other properties of the rubber such as tensile strength and tear are beginning to deteriorate and, in fact, the compound is overloaded. It seems reasonable to assume, therefore, that the optimum loading for a bond is of exactly the same character as loading for any other property.

If a series of tests is made on bonded articles with the rubber in shear, and rubbers which increase progressively in the loading of a particular filler are used, it will be found that, although the breaking loads increase progressively, the elongation at break is almost the same. Some of this uniformity is undoubtedly due to the change in slope of the stress-strain curve at high loads, but it does seem as if the bond strength depends to some degree on the extent to which the rubber will deform.

The falling-off in bond strength as rubber is softened is not, in practice, such a disadvantage as it might appear. Rubber-metal articles are usually designed to give a certain deformation under a specified load, and soft rubbers are used to give this deformation under light loads. It is obviously an advantage to have the bond strength as high as possible, for safety, but the idea of designing articles for a maximum permissible deformation is useful, and quite as reasonable as specifying a bond strength.

It must not be thought that a low bonding power in rubber can be made good by altering the solution or "tie-gum" applied to the brass surface. Such solutions can certainly modify the bond, but the effect is only to modify the main character of the bond being decided by the bulk of the rubber.

Examples may make this clear. Thus, rubbers cured with tetramethylthiuram disulfide, without free sulfur, do not bond to brass plate. The application of a sulfur-bearing solution between rubber and plate makes no difference at all; there is still no bond. Conversely, a sulfur-bearing rubber bonds perfectly, even if the solution is without sulfur. This effect is, of course, due to migration of sulfur, but the effect is quite general.

Again, if the bond strength is affected by the amount of deformation of the rubber, the effect of a thin coat of solution is negligible. It is seen, therefore, that, on the whole, the solution has only a secondary effect.

The highest breaking load that can be obtained is when the rubber breaks first, and this is generally not more than about one-third of the breaking strength of the same rubber tested in the usual way. This, unfortunately, seems unavoidable, and is due to the high extension of the rubber. The rubber away from the bond can contract laterally, but that near the metal cannot contract and is, therefore, stressed in two directions at once. Under these conditions, a lower breaking load is to be expected.

## CHARACTERISTICS OF WILD RUBBERS \*

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A brief examination of a group of five wild African rubbers, specimens of which have been kindly furnished by G. Martin, has been made, and has given the information set out below. For purposes of comparison corresponding observations for *Hevea* rubber, balata and a specimen of Malayan *Ficus elastica* are appended.

**Composition.**—The analytical details of the African rubbers are shown in Table 1 (Nos. 1–5) and of the non-African specimens (Nos. 6–8). The first three specimens were received in the form of dark-colored creped sheets, whereas Nos. 4 and 5 were, respectively, hard and soft resinous materials, quite unlike crude *Hevea* rubber in physical characteristics; the rubber contents of the first three specimens were high; those of Nos. 4 and 5 were low. Specimen No. 8 was also in sheet form, and had a high rubber content.

TABLE 1

No.	Species	Acetone Extract (%)	Protein Approx. (%)	Rubber Approx. (%)	Hydrocarbon				
					N (%)	C (%)	H (%)	C/Hx z	Iodine value
1.	<i>Funtumia</i>	7.75	7.7	84.5	1.26 1.30	83.75 83.30	11.50 11.20	8.1	324
2.	<i>Clitandra</i>	5.15	2.3	92.5	0.39	86.20 86.15	11.55 11.60	8.0	348
3.	<i>Landolphia</i>	7.70	0.7	91.6	0.11	85.9 85.25	11.5 11.35	7.95	347
4.	<i>Ficus platyphylla</i> (Red kano)	84.0	1.3	ca.11	0.23	85.7 85.55	11.7 11.8	8.1	344
5.	Niger paste	65.0	4.3	ca.6.6	0.73	84.1	11.5	8.1	332
6.	Crepe rubber ( <i>Hevea</i> )	2.9	2.1	94.0	0.35 0.4	87.4	11.7	7.95	358
7.	Balata (twice pptd.)	...	...	...	...	86.4	11.8	8.1	371
8.	<i>Ficus elastica</i>	3.75	1.0	94.2	0.17	86.9 86.7	11.95 11.75	8.15	364

The resins extracted by acetone from the first three species bore a close superficial resemblance to those normally obtained from *Hevea* rubber; that extracted from *Ficus platyphylla*, representing 84 per cent of the whole, consisted mainly (at least 60 per cent) of crystalline water-insoluble nonacidic material of unsharp melting point (135–140°C), with a smaller amount of semitransparent resin which partly crystallized on long standing. Two fractions of the crystalline resin, crystallized from acetone, gave the analytical figures: (m.p. 143°) C 81.5, H 11.65; (m.p. 135°) C 81.45, H 11.3 per cent. Compared with *Hevea* rubber, the nitrogen content of the acetone-extracted *Landolphia* rubber was unusually low, and the extracts of the extracted *Funtumia* and Niger-paste rubbers were unusually high; the protein content as

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estimated on the usual basis of 6 times the nitrogen content varied accordingly. The Niger paste consisted mainly of water (about 33 per cent) and water-clear, noncrystalline, nonacidic resin.

Taking into consideration the fact that the specimens had not been freed from nitrogen and traces of oxygen, the carbon/hydrogen ratio in each case agrees fairly satisfactorily with the formula  $(C_5H_8)_n$ . The iodine values also differ but little from those shown by good-quality crepe rubber, and hence are consistent with a polyisoprenic constitution.

**Molecular weight.**—Molecular weights were measured by the methods already described<sup>1</sup>, viscosities being determined in benzene solution, and osmotic pressures in benzene plus 15 per cent methyl alcohol. The following values were found for  $10^{-5}$  M, where M is the molecular weight.

(a) VISCOSITY:	(1) <i>Funtumia</i>	3.0	(2) <i>Clitandra</i>	2.85
	(3) <i>Landolphia</i>	2.35	(4) <i>Ficus platyphylla</i>	1.65
	(5) <i>Niger paste</i>	2.4	(6) <i>Ficus elastica</i>	3.3
(b) OSMOTIC:	(2) <i>Clitandra</i>	2.35	(3) <i>Landolphia</i>	1.8

These values are to be compared with those obtained by Gee<sup>1</sup> for *Hevea* rubber: (1) 3.45, (2) 2.6. Staudinger and Fischer<sup>2</sup> have reported significantly lower molecular weights, determined osmotically in toluene, for gutta (1.2) and balata (0.9). Wolff<sup>3</sup> found in the same way a still lower value for gutta (0.3).

**Physical properties.**—The preparation and examination of films prepared from benzene solution were carried out by methods described elsewhere<sup>4</sup>. Observations were limited to those properties which seemed most characteristic of *Hevea* rubber, i.e., the elastic extensibility and tension, and the phenomena associated with crystallization.

The tensile data are given in Table 2, in which the elongations marked with an asterisk represent nearly, but not accurately, the maximum elongation obtainable at 25° C.

TABLE 2  
TENSILE DATA AT 25°C

Rubber	Elongation (percentage)	Tension at constant length on actual section (Instantaneous extension)	
		After 5 sec. (kg. per sq. cm.)	After 15 min. (kg. per sq. cm.)
<i>Clitandra</i>	470	26.5	19.2
	650	71	59
	790*	180	167
<i>Funtumia</i>	530*	159	147
<i>Landolphia</i>	880*	190	164
<i>Ficus elastica</i>	750*	...	...
<i>Ficus platyphylla</i>	100*	...	...

*Ficus platyphylla* was extremely weak. The remaining rubbers, including *Ficus elastica*, for which data were not recorded, showed tensile properties closely resembling those of *Hevea* rubber, with the exception of *Funtumia*, which was rather less extensible.

When stretched to a high elongation at 25° C, all the above rubbers except *Ficus platyphylla* retained practically their full elongation until warmed to a temperature close to 30° C, when retraction temperatures were: *Clitandra* (650 per cent) 30° C, (790 per cent) 30° C; *Funtumia* (530 per cent) 30.5° C; *Landolphia* (890 per cent) 30.5° C. Under the same conditions, *Hevea* re-

tracted at 29.5° C. *Ficus elastica* behaved similarly, but precise measurements were not made.

As the retraction temperatures may be regarded as the effective melting point of the crystals formed on extension, the evidence suggests that the crystals formed in *Clitandra*, *Funtumia* and *Landolphia*, and probably also in *Ficus elastica*, are identical with those in *Hevea*.

In its low extensibility and strength, and absence of crystallization either in the unstretched or stretched state, *Ficus platyphylla* behaved like a low-molecular *Hevea* rubber<sup>5</sup>. It certainly was not, as one of its local names, Niger gutta, implies, a gutta, as gutta exists normally in the crystalline state. The general conclusion is that all the materials examined have the properties to be expected in a *Hevea* rubber of the same molecular weight.

TABLE 3  
OBSERVED SPACINGS (in Å)

Layer line	<i>Hevea</i>	<i>Clitandra</i>	<i>Landolphia</i>	<i>Funtumia</i>	<i>Ficus elastica</i>
0	6.30 s 4.22 vs 3.11 m 2.24 m 2.11 vw	6.2 4.22 3.11 2.24	6.3 4.28 3.08	6.3 4.22 3.08	6.3 4.22 3.08
1	5.47 vw 4.98 s 3.76 s 3.45 w 2.88 vw 2.54 m 2.05 vw	4.93 3.75   2.57	5.00 3.71	4.95 3.75	4.95 3.75
2	4.10 m 3.70 w 3.42 s 3.00 m 2.75 m 2.40 w 2.07 vw 1.92 vw	4.10 3.40 2.75 2.44	4.10 3.40	4.10 3.40	4.10 3.40

Note.—Data for *Hevea* are for a hydrocarbon obtained by fractionation; s denotes a strong spot, m moderate, w weak.

**X-ray examination.**—Specimens 1–4 and 8 were examined by x-rays, and all were found to give the amorphous halo characteristic of *Hevea* rubber. When stretched, all except *Ficus platyphylla* gave fibre diagrams similar to that of stretched *Hevea* rubber, as will be seen from the comparative data given in Table 3. Crystallization was not so complete in the African rubbers, and consequently only the stronger of the spots obtained with *Hevea* were observed. The failure of *Ficus platyphylla* to give fibre diagram means simply that it could not be stretched sufficiently to produce crystallization: a similar phenomenon has been found with *Hevea* rubbers of low molecular weight.

The identity of the diffraction patterns leaves no doubt that all these specimens consist essentially of the same rubber hydrocarbon. It is of interest also to note that additional reflections were obtained from *Funtumia*: these appear to be similar to those reported by Schallamach<sup>6</sup> for *Hevea*, and shown by him to originate from impurities.

*Conclusion.*—The work leads to the conclusion, which can be stated with considerable confidence, that the rubbers examined are without exception polyisoprene rubbers, identical in their chemical constitution, and, when purified, similar in physical characteristics, to ordinary *Hevea* rubber.

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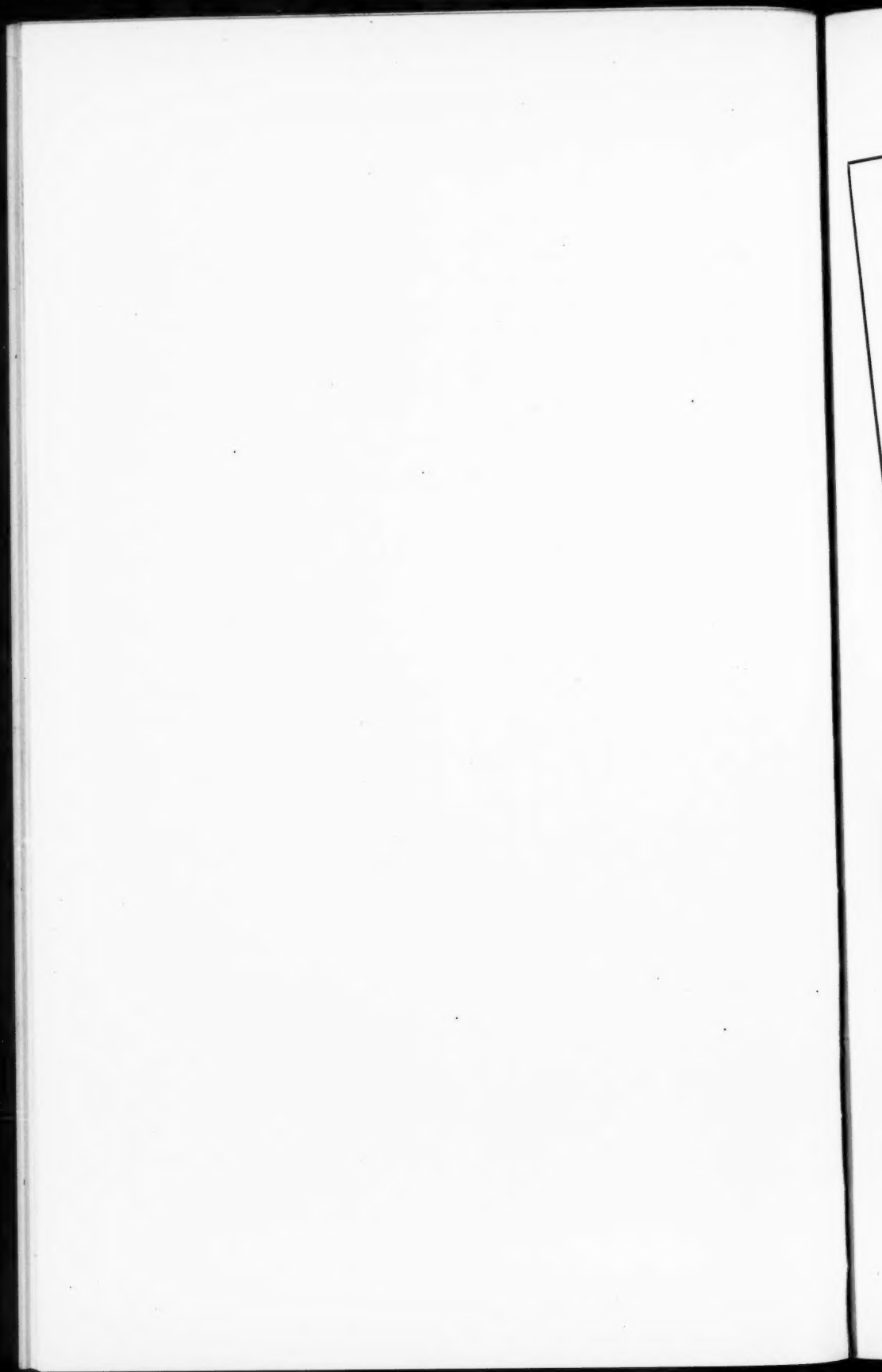
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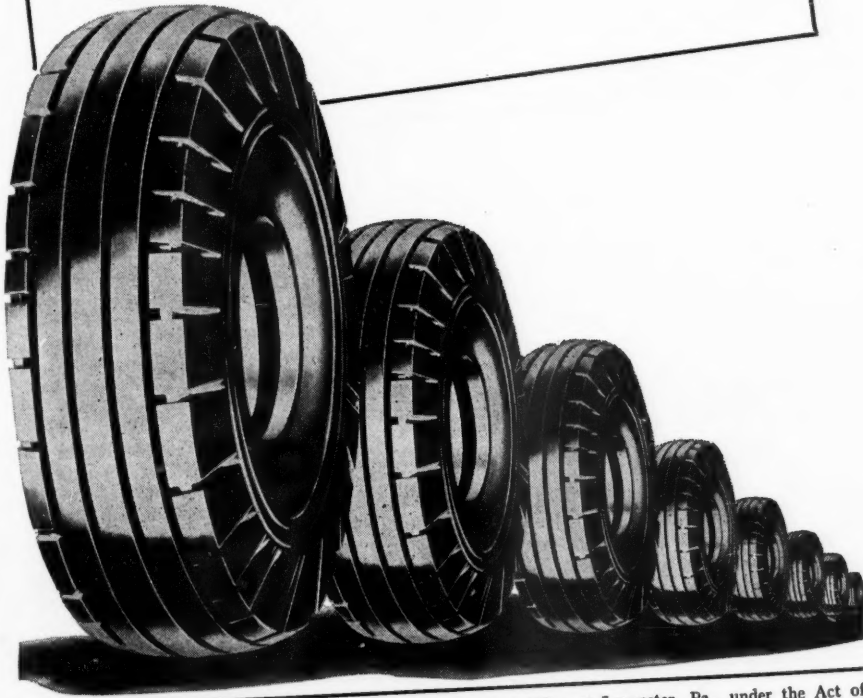
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Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in the Act of February 28, 1925, embodied in paragraph 4, Section 538, P. L. and R., authorized September 25, 1940.





New data on the effects of M.R. on the physical properties of GR-S products has been gathered after extensive tests by Wishnick-Tumpeer's laboratory and is now available in the booklet illustrated above—"WITCO M.R. in GR-S (BUNA S)."

Among the results that can be obtained with WITCO M.R. in a typical tire tread stock formula is increased resistance to growth of cracks due to flexing. In addition, the following results can be achieved:

*Making the uncured stock more plastic and therefore easier to process*

*Increased tensile strength*

*Increased tear resistance*  
*Decreased elongation obtained at break*  
*Decreased effect of aging on lowering tensile strength, lowering elongation and hardening the cured stock*  
*Decreased modulus*  
*Increased tensile product*  
*Decreased resilience*

The booklet also presents information on the properties that may be obtained by using larger amounts of channel black and sulfur in conjunction with various amounts of M.R.

A copy of "WITCO M.R. in GR-S (BUNA S)" is yours for the asking. Your request will receive our immediate attention.

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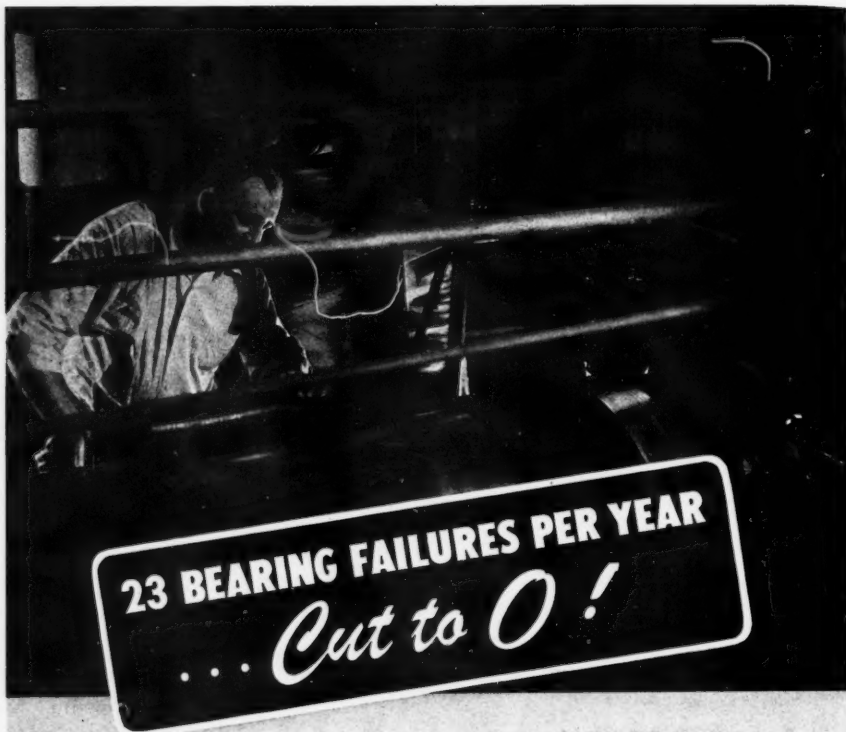
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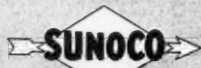
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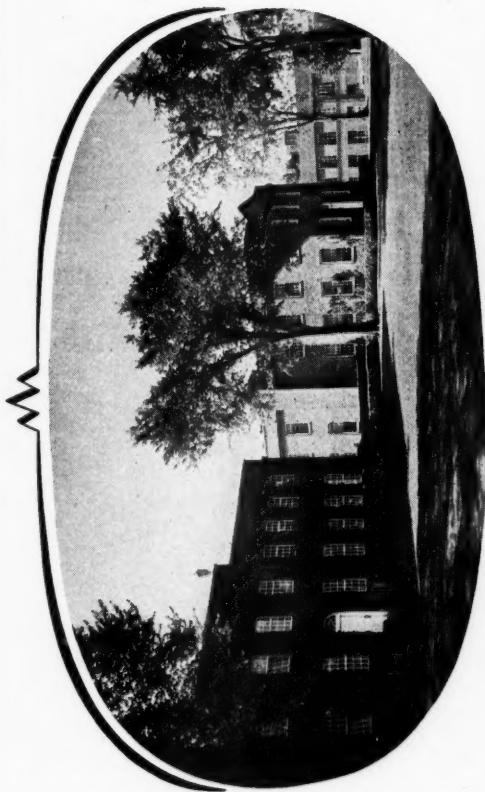
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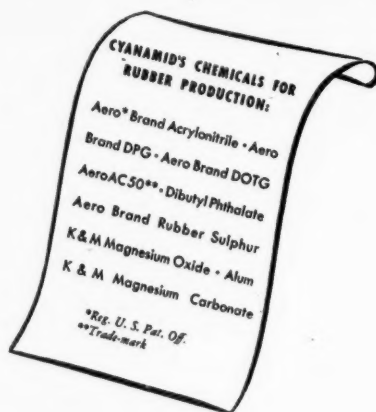
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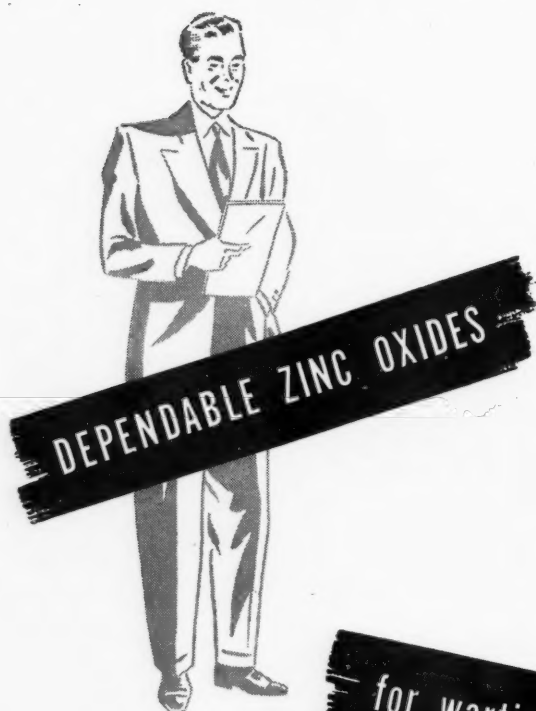
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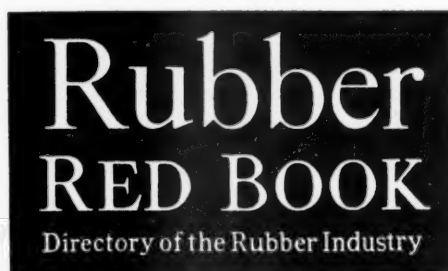


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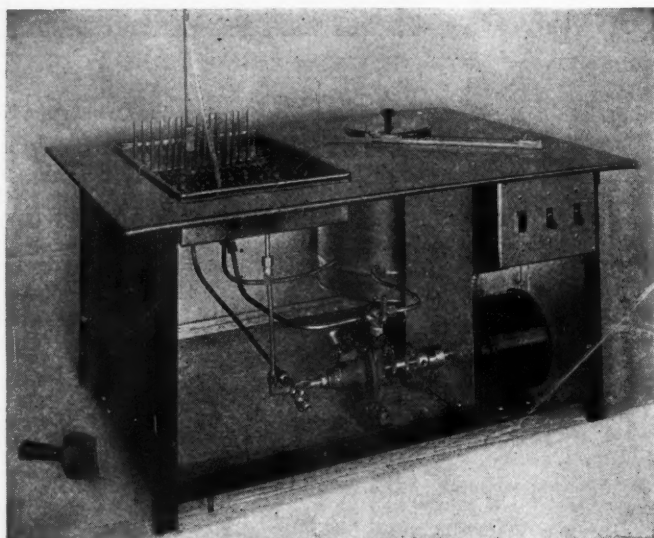
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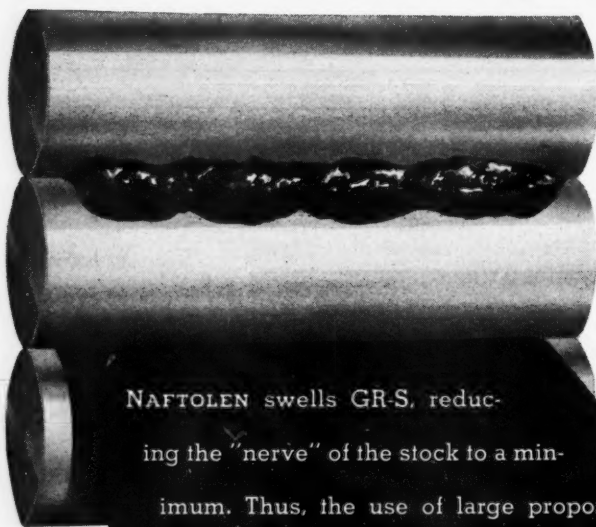
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# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XVI

NUMBER 4



October, 1943

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